REMOVAL OF ARSENIC FROM NEWFOUNDLAND WATER USING IMPREGNATED PEAT

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Removal of Arsenic from Newfoundland Water Using Impregnated Peat

By

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Abstract

Arsenic exists naturally and it is the 20th most abundant element in the earth's crust. The high Arsenic concentration in some of Newfoundland water sources could be due to the oxidation of Arsenic bearing minerals by the heavy precipitations and rain fall all over the year. Arsenic is carcinogenic and the United States Environmental protection agency and the Canadian Environmental Quality Guidelines limit set is 10 μg/l of Arsenic in drinking water. The main objective of this research was to find a cheap, efficient, and locally available material in Newfoundland that could remove Arsenic from water. Peat is an abundant material in Newfoundland, however, functional groups, which are the main constituent of peat do not react with Arsenic species. To improve peat properties, Fe was used to impregnate peat, react with the functional groups, get oxidized, and the impregnated Fe hydroxide and oxyhydroxide could then adsorb Arsenic. To detect the properties of horticultural peat, characterization tests were carried out for the untreated and impregnated peat. In addition, batch and column studies were conducted to test the peat capacity for Arsenic adsorption before and after impregnation. It was found that peat impregnated with 0.54 M ferrous chloride (Fe 0.54-Peat) was the best adsorbent and it could reduce the Arsenic level from 60 μg/l to less than 10 μg/l. A total of 9 liters were treated with Fe 0.54-Peat in a continuous flow system to a level below this one. The pH increased with the duration of the experiments, as conditions gradually become more reducing and the pH was the main factor controlling the Arsenic adsorption between pH 3 to 5. The two suggested mechanisms responsible for adsorption are inner sphere complex and coadsorption or a mix between ion exchange and complexation.

Table of contents

Acknowledgement ii

Abstract iii

List of Symbols vii

List of Abbreviations viii

List of Figures xi

List of Tables xiii

Chapter 1 Introduction

1.1 The Arsenic Problem in Newfoundland 1

1.2 Background 4

1.3 1.2.1 Factors Affecting Arsenic Release 5

1.2.2 Arsenic Removal Techniques and Efficiencies 7

1.2.3 Selected Mechanism and Material 12

1.3 Objective 13

1.4 General Outline 14

Chapter 2 Theoretical Background

2.1 Arsenic and Metal Removal by 16

2.2 Arsenic Speciation and Adsorption 19

2.3 Peat Characteristics 24

2.4 Peat Impregnation 28

2.5 Factors Affecting Arsenic Retention by Activated Carbon 31

2.6 Factors Affecting Impregnation Efficiency 38

2.7 Precipitation, Dissolution, and Desorption 40

2.8 Minitab 40

2.9 Detecting Arsenic Levels 42

Chapter 3 Materials, Methods, Tools and Equipment

3.1 Materials 46

3.1.1 Iron 46

3.1.2 Oxidizer 47

3.1.3 Acids and Bases 47

3.1.4 Arsenic 48

3.2 Characterization Tests 48

3.2.1 Point of Zero Charges Measurement (PZC) 48

3.2.2 Cation Exchange Capacity Measurement (CEC) 50

3.2.3 Acid Digestion 51

3.3 Dry Weight Experiment 51

3.4 Method for Peat Impregnation 51

3.5 Batch and Column studies 52

3.6 Arsenic Detection with ICP-MS and Test Kit 58

3.7 Minitab 59

Chapter 4 Results

4.1 Characterization Results 61

4.1.1 Point of Zero Charges 62

4.1.2 Cation Exchange Capacity 73

4.1.3 Acid Digestion 74

4.2 Dry Weight Results 76

4.3 Batch Test Results 78

4.3.1 The La Motte Arsenic Test Kit Results 78

4.3.2 ICP-MS Results 80

4.3.3 Comparison Between the Arsenic Test Kit and ICP-MS Results for Batch Tests 85

4.4 Column Test Results 87

4.4.1 Column Test for Untreated Peat 87

4.4.2 Column Test for Fe 0.54-Peat 89

4.4.3 Acid Digestion for the Fe 0.54-Peat After the Column Test with Spiked Arsenic Influent 93
4.4.4 BlankColumn test for Fe 0.54-Peat 94

4.5 Statistical Analysis Results 97
4.5.1 Analysis of Newfoundland Water Sources 97
4.5.2 Parameters Correlated with Arsenic in Newfoundland Water and Global Wide 97

Chapter 5 Conclusion and recommendation

5.1 Conclusion 105
5.2 Recommendation 110
5.3 Future Research 112

Appendix

A.1 Calculations 113
A.2 Permission of Author and Publisher for the use of Tables and Figure 115
A.3 Tables 116
A.3.1 Correlation of Arsenic Level with Physical Properties and Chemical Parameters of Newfoundland Water Resources 116
A.3.2 The Data Obtained from the PZC Experiments 125

List of Symbols

°C	Degree Celsius
cmol	Centimoles
d*f*	Degree of freedom
µg	Micrograms
g	Grams
H^+	Hydrogen ion
Ka	Dissociation or ionization constant
Kg	Kilogram
l	Liter
mg	Milligrams
ml	Milliliter
mmol	Millimoles
mol	Mole
mequ	Milliequivalent
N	Normal
OH^-	Hydroxyl ion
pH	- log $[H^+]$
pKa	- log Ka
[ ]	Concentration

List of Abreviations

AA	**Activated Alumina**
AAS	**Atomic adsorption spectrometer**
AC	**Activated carbon**
As	**Arsenic**
As III	**Arsenite**
As V	**Arsenate**
Ag	**Silver**
CEC	**Cation exchange capacity**
Cd	**Cadmium**
CHC	**Coconut husk carbon**
CICHC	**Cu impregnated coconut husk carbon**
Cr	**Chromium**
Cu	**Copper**
DDL	**Double diffused layer**
DO	**Dissolved Oxygen**
DOC	**Dissolved Organic Carbon**
Fe	**Iron**
Fe 1.08-Peat	**Peat impregnated with 1.08 M Fe**
Fe 0.54-Peat	**Peat impregnated with 0.54 M Fe**
Fe 0.108-Peat	**Peat impregnated with 0.108M Fe**
Fe 0.054-Peat	**Peat impregnated with 0.054 M Fe**

Fe-Peat	**Iron impregnated peat**
FeAC	**Iron impregnated activated carbon**
GAC	**Granular Activated Carbon**
GFAA	**Graphite furnace atomic adsorption**
Hg	**Mercury**
ICP-ES	**Inductively coupled plasma emission spectroscopy**
ICP-MS	**Inductively coupled plasma mass spectroscopy**
IOCS	**Iron oxide coated sand**
M	**Molar**
N	**Normal**
Ni	**Nickel**
Pb	**Lead**
pH_{PZC}	**pH of the point of zero charges**
POE	**Point of entry**
POU	**Point of use**
ppb	**Part per billion**
ppm	**Part per million**
PZC	**Point of zero charge**
RPC	**Research and Productivity Council**
Sb	**Antimony**
SSA	**Specific surface area**

U.S. EPA	**United States Environmental protection agency**
VOC	**Volatile organic carbon**
Zn	**Zinc**

List of Figures

Figure	page number
Figure 2.1 Suggested structure of fulvic acid	27
Figure 2.2 Carboxylic and phenolic groups impregnation with iron	34
Figure 2.3 Fe^{2+} replacing H^{+}	35
Figure 2.4 Oxidation of Fe^{2+} to Fe^{3+}	36
Figure 2.5 Adsorption of Arsenic	37
Figure 3.1 Column used for column test	55
Figure 3.2 Components of the column used	56
Figure 4.1 Titration curve for determining ZPC for untreated peat	62
Figure 4.2 Zooming on the area of intersections of untreated peat curve	63
Figure 4.3 Titration curve for determining ZPC of peat impregnated with 1.08 M Fe (Fe 1.08-Peat)	64
Figure 4.4 Zooming on the area of intersections of 1.08 Fe-Peat	65
Figure 4.5 Titration curve for determining ZPC of peat impregnated with 0.54 M Fe(Fe 0.54-Peat)	66
Figure 4.6 Zooming on the area of intersections of Fe 0.54-Peat	67
Figure 4.7 Titration curve for determining ZPC of peat impregnated with 0.108 M Fe (Fe 0.108-Peat)	68
Figure 4.8 Zooming on the area of intersections of Fe 0.108-Peat	69
Figure 4.9 Titration curve for determining ZPC of peat impregnated with 0.054 M Fe (Fe 0.054-Peat)	70

Figure 4.10 Zooming on the area of intersections of Fe 0.054-Peat 71

List of tables

Table	page number
Table 1.1 Efficiencies and Prices (where available) for various Arsenic removal techniques	11
Table 2.1 Functional group in fulvic and humic acid	17
Table 2.2 As speciation in aqueous solution at different pH levels	21
Table 2.3 CEC and SSA of different kinds of peat	24
Table 2.4 The effect of pH on the peat charge and As and Fe uptake	32
Table 2.5 Pearson's Correlation	42
Table 4.1 PZC of untreated and impregnated peat	72
Table 4.2 Cation exchange capacity for natural peat and the four impregnated peats	73
Table 4.3 Acid digestion results for five peat soil samples	75
Table 4.4 Dry weight of peat	77
Table 4.5 Arsenic test kit results for the batch tests	80
Table 4.6 ICP-MS results for the batch tests	82
Table 4.7 Comparison between Arsenic Kit and ICP-MS Results for Batch test	86
Table 4.8 Concentration of elements in the effluent of the untreated peat column	87
Table 4.9 Concentrations of elements in the effluent of the Fe 0.54-Peat column	90
Table 4.10 Correlation between pH, Arsenic and other elements concentrations in column effluent before compaction	91

Table 4.11 Acid digestion of Fe 0.54-Peat after the column test with spiked Arsenic influent 93

Table 4.12 Concentrations of elements in the effluent of blank column test of Fe 0.54-Peat 95

Table 4.13 The correlations between Arsenic, pH and other elements in the effluent of the blank column test before compacting Fe 0.54 peat during the blank test 96

Table 4.14 Significant correlations of physical properties and chemical parameters with Arsenic 98

Table 4.15 Parameters correlated with Arsenic in different locations affected by Arsenic problem 101

Table A.2 Provincial correlations 116

Table A.3 Central region correlations 119

Table A.4 Eastern region correlations 121

Table A.5 Western region correlations 123

Table A.6 Titration table for determining the PZC for the untreated peat 125

Table A.7 Titration table for determining PZC of peat impregnated with 1.08 M Fe 126

Table A.8 Titration table for determining PZC of peat impregnated with 0.54 M Fe 127

Table A.9 Titration table for determining PZC of peat impregnated with 0.108 M Fe 128

Table A.10 Titration table for determining PZC of peat impregnated with 0.054 M Fe 129

Table A.11 Detected Metals in peat and their concentrations 130

Chapter one

Introduction

1.1 The Arsenic Problem in Newfoundland

Groundwater sources represent fifty percent of Newfoundland water resources. Such sources provide water for drinking and domestic uses for people mostly in rural areas. Water analysis of different wells has revealed that many of them are having high Arsenic (As) contents. Accordingly, contaminated wells should be treated or abandoned for other sources. Choosing between the two alternatives depends on the cost of each, yet digging other wells might not be the perfect solution due to the risk of contamination in the new source (Guzzwell, 2006).

According to the information and data obtained from Newfoundland and Labrador Department of Environment and Conservation, there are 536 different water sources in Newfoundland, half of which are groundwater and the other half are surface water sources. A total of 128 samples from 52 sources were analyzed for physical and chemical properties. For some of the sources, samples were taken in different seasons or years. 100 samples were taken from groundwater sources while 28 were taken from surface water sources. 87 samples were taken from 26 sources in the eastern region and the Avalon Peninsula, the most populated area in the province, 16 samples were taken from 10 sources in central Newfoundland, and 25 samples were taken from 16 sources in the western region (Guzzwell, personal communication, 2006; Rageh et al., 2007)

The analysis showed that only 3 out of 52 sources had Arsenic concentrations below the 10 µg/l recommended limit in Canada. In the eastern part of the province, especially in the Avalon Peninsula, the number of contaminated wells and the Arsenic concentrations in water were higher for the rest of the province. Although wells exceeding the 10 µg/l limit for arsenic are not used as sources of water unless they are treated, the government is looking for a more economical method for treatment and Arsenic removal (Guzzwell, 2006; Rageh et al., 2007).

Arsenic sources can be described as natural or anthropogenic. Natural Arsenic sources are forest fires, weathering and volcanoes (Piver, 1983; Burton, 1987). On the other hand, anthropogenic sources include those where Arsenic is released from pesticides, herbicides, or wood preservatives, and during the mining and processing of ores for

minerals such as nonferrous ores containing Cu, Pb, Zn, Au, and Ur (Lorenzen et al., 1995; Piver, 1983). Urban runoff has been estimated as the largest source of Arsenic in surface water bodies.

The release of Arsenic due to the oxidation of polymetallic sulfide ores or under harsh reducing conditions are examples of weathering (Pokonova, 1998; Robinson et al., 2006). Arsenic is the 20th most abundant element and its concentration is not high in the earth crust. It is about 1.7 mg/kg, however, the main contributing sources for Arsenic release are natural (Robinson et al., 2006). There are more than 300 minerals containing Arsenic (Lorenzen et al., 1995).

There are two main types of rocks in Newfoundland, igneous and sedimentary. Igneous rocks have Arsenic concentrations ranging from 0.2-13.8 mg/kg. Sedimentary rocks existing in Newfoundland are shale, limestone, and sandstone which have Arsenic concentrations of 0.3-500, 0.1-20, and 0.6-120 mg/kg respectively (Allard, 1995). Sulfide minerals are the main Arsenic bearing formations. They are abundant in mafic lavas and igneous rocks in Newfoundland (Swinden, 1988). "Arsenic bearing minerals in Newfoundland include arsenopyrite (FeAsS), realgar (AsS), orpiment (As_2S_3), niccolite (NiAs) and cobbalite (CoAsS)" (Rageh et al., 2007). In Table A1 on the CD attached the concentration of Arsenic as well as other elements and metals in different places in Newfoundland are presented.

1.2 Background

Arsenic has four oxidation states which are +3, +5, 0 and – 3. The most common oxidation states are -3 or Arsenides, +3 or Arsenites, +5 or Arsenates, and sometimes arsenic bonds to itself forming As-As pairs as in Realgar (Wikipedia, 2008, Lorenzen et al., 1995). In the aqueous phase, it exists as Arsenate or As (V) and Arsenite or As (III). The latter is more mobile and toxic (Lorenzen et al., 1995). Arsenic forms can be described in many different ways. They can be organic and inorganic forms, or volatile, solid, and aqueous forms. Arsenic can change from one form to another depending on its source and surrounding conditions. Microorganisms in soil, sediments, and water can produce volatile organic arsenic, which enters the atmosphere and becomes transformed into an inorganic form. Soluble As (III) can be oxidized and transformed into the insoluble As (V) that can be adsorbed to sediments or soil and these transformed to solid phase minerals (Environment Canada, 2002).

In many countries, the presence of Arsenic in groundwater is correlated with the presence of Fe, Mn, Cu, Ni, Cr, and Co. Cations are ions with positive valence while anions are ions with negative valence. Major ions are ions of concentration higher than 1 mg/l. In Newfoundland groundwater major cations include Ca^{2+}, Mg^{2+}, Na^{+}, and $K^{+}HCO_3^{-}$ while major anions include CO_3^{2-}, SO_4^{2-}, Cl^{-}, NO_3^{-}, and Si^{-4}. On the other hand, minor ion concentrations in groundwater depend on the residence time or the contact of solution with solid phase or surfaces. Minor cations include Fe^{2+}, Mn^{2+}, Al^{3+}, Ba^{2+}, Cd^{2+}, Cr^{3+}, Pb^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, As^{3+}, $P^{3+}$and Hg^{2+} while minor anions include Br^{-}, Se^{-2}, and F^{-}.

Oxidation and reduction reactions, adsorption, desorption, precipitation and dissolution are the main reactions controlling the retention, release and mobility of elements and ions in water (Deutsch, 1997).

Finding cheap treatment techniques and materials for Arsenic has been the issue of different studies for a long time. Basically, materials used for treatment should be abundant, cheap, and available close to the location of contamination. Adsorption was described as one of the best available technologies for Arsenic removal (Pokonova, 1998). Finding a better adsorbent of higher affinity for Arsenic is very important for the imposed higher standards by health and environmental organizations.

1.2.1 Factors Affecting Arsenic Release

The redox potential (Eh) is a measure of the oxidation and reduction state, and the higher the oxidation state the higher the redox potential. However, oxidation does not depend only on the presence of oxygen since some reactions involve hydrogen ions, accordingly, such reactions are pH dependent. For example, protonation increases at lower pH which increases the oxidation state. Solubility of elements depends on the redox potential and pH. Solubility is the amount of a substance in moles/liter or mg/liter that can dissolve in a solution under a given set of conditions (Snoeyink et al., 1980, p 249). Adsorption and desorption occur as a result of ion exchange and surface complexation. Organic materials and the organic content of a soil play a great role in ion exchange and complex formation (Deutsch, 1997).

Precipitation and dissolution are the results of disequilibrium between the solid and the liquid phase. Weathering is the result of disequilibrium between rocks and rain or snow, which results in the release of minerals, or dissolution, and the presence of secondary or minor minerals in the groundwater. Rain can also help in the oxidation of the Arsenic bearing minerals which contain sulfides as well as causing the release of Arsenic and the presence of sulfates at high concentrations in groundwater (Rageh et al., 2007). The degree of precipitation and dissolution depends on the ion activity versus the equilibrium constant and on the residence time of the liquid phase within the solid matrix. Precipitation occurs when the saturation index is more than zero or when ion activity is higher than the equilibrium constant and vice versa for dissolution (Deutsch, 1997).

As (III) and As (V), the most common forms of Arsenic in groundwater, are stable under reducing and oxidizing conditions respectively. Under oxidizing conditions, Arsenic combines mainly with Fe forming scorodite, $FeAsO_4 \cdot 2H_2O$, which limits Arsenic mobility. On the other hand, under reducing conditions Arsenic combines with the sulfide minerals such as Realgar (AsS) and Orpiment (As_2S_3) which reduce Arsenic concentration and mobility. Oxides and oxyhydroxides are the best adsorbents for Arsenic (Deutsch, 1997).

Under oxidizing conditions, arsenate will be efficiently adsorbed on oxide surfaces at a pH close to 4 while adsorption of arsenite will be favored at higher pH. The presence of antimony, silica and phosphorus affects the adsorption of arsenic since they compete for

the same sites. Phosphate can also affect the pH range over which As (III) will be adsorbed causing preferential adsorption of As (III) over As (V) (Dixit and Hering, 2003; Ngo et al., 2002).

The software package used for finding correlations between the Arsenic concentration and other elements, metals, parameters and physical properties was Minitab. Minitab is a statistical software package that provides a wide range of basic and advanced data analysis options which help organize and analyze data and report results (University of Calgary, information technology, 2008). The program was developed at Pennsylvania State University in 1972 by Barbara Ryan, Thomas Ryan, Jr. and Brian Joiner (Wikipedia, 2008). The Data provided by Newfoundland and Labrador Department of Environment and Conservation was statistically analyzed using Minitab to study and determine the possible reasons for Arsenic release in Newfoundland.

1.2.2 Arsenic Removal Techniques and Efficiencies

Treatment technologies for Arsenic include ion exchange, precipitation, sorption and membrane processes. Selecting among these technologies depends on the water quality of the source, the presence of other contaminants, the pH of the water, the cost of treatment, and the community served by the source. According to tests conducted in September 2002 by Research and Productivity Council (RPC), Fredericton, New Brunswick, the dominating species present in groundwater was As (V) in wells on the Avalon peninsula (Government of Newfoundland and Labrador, 2006).

Most of the adsorbents used for Arsenic removal are oxide based. Activated alumina, iron oxide coated sand, granular ferric hydroxide, and granular activated carbon depend on the presence of oxides and oxyhydroxides that retain Arsenic by a process called ligand exchange. Ligands are lone pair donor ions (lewis bases) attached to a central metal ion by strong covalent bonds. Activated alumina can be regenerated by adding NaOH yet 2 % will be dissolved while other iron-based adsorbents are generally replaced after exhaustion (Subramaniam et al., 1997).

Ion exchange is another mechanism used for Arsenic removal. Different resins are commercially available and are used for such purposes. Selectivity of resins used to treat Arsenic are as follow: SO_4^{2-}> $HAsO_4^{2-}$ > CO_3^{2-} > NO_3^- > Cl^- > $H_2AsO_4^-$ > HCO_3^- > H_3AsO_3. As (V) is easily removed and it is preferentially adsorbed over As(III). Resins exchange the attached Cl with Arsenic and they can be regenerated by backwashing using NaCl (Bissen et al., 2003).

Precipitation is another technique in which a coagulant such as aluminum ferric chloride or ferric sulfate is added to wastewater in the presence of lime, to increase pH, and flocculate and settle small particles. The coagulant used gets hydrolyzed and precipitates, however, some of the alum coagulant remains as a soluble complex increasing the percentage of aluminum in the effluent. Adding coagulants to Arsenic contaminated water causes them to hydrolyze. This step is followed by complex formation between metal oxides and Arsenic. The removal efficiency of iron-based coagulants is more than that of the aluminum ones. The percentage of Arsenic removed depends on its speciation.

90 % removal of As (V) is typically achievable versus 60 % removal for As (III) at a pH value between 6 and 8. Accordingly, oxidizing agents such as chlorine or potassium permanganate are used to oxidize As (III) to As (V) (Jiang, 2001).

Inorganic divalent ions interfere with the coagulation process. Sulfates decrease the removal of Arsenic at pH 5 and their effect decreases gradually as the pH increases. In contrast, calcium increases Arsenic removal with the increase in pH value, which explains the increase in Arsenic uptake when adding lime softening. Lime raises the pH and helps the co-removal of Ca^{2+}, Mg^{2+}, and iron oxides together with Arsenic (Han et al., 2002).

Coagulation can also be used with micro filters where iron based coagulants are used to oxidize Arsenic to decrease its mobility and solubility. The solution is then pressurized through a 0.2 to 1.2 μm semi permeable membrane to separate the unsettled parts. There are other membrane processes that can be used, yet, they differ in the operating pressure and the filter size (Bissen et al., 2003).

Ultrafiltration as microfiltration has low operation pressure and can remove suspended particles yet it is not effective in removing dissolved solids. Arsenic the pH value increases the efficiency of both techniques is reduced. Nanofiltration and reverse osmosis can remove dissolved matter. The later is also used for making salty water poTable, however, a lot of water is wasted through such a process. Both latter techniques are efficient in Arsenic removal, which can reach up to 90 % (Bissen et al., 2003).

For smaller communities of 10,000 persons, point of use (POU) or point of entry (POE) devices may be installed in water outlets and taps or at points of entries respectively. Due to their simplicity, efficiency, and the advantage of removing As (III) better than membrane techniques, adsorption is the mechanism used for POU and POE devices. Adsorbents can be placed in disposal bags that are dipped in water or they can be installed in water supply systems or pipes (Gilles and Mathis, 2002).

If other available sources have lower Arsenic concentration than the one in use, the contaminated source will be abandoned. Sometimes blending two sources to reach low accepTable concentrations can be considered an option (Guzzwell, personal communication, 2006)

Commercially available and common adsorbents are activated alumina (AA), granular activated carbon (GAC), and iron oxide coated sand (IOCS). AA has low efficiency for Arsenic removal (51 %) while GAC and IOCS has very high efficiency that reaches up to 96%. For ion exchange, the use of a cationic resin can remove 40 to 90 % (average 65 %) of Arsenic. Nanofiltration and reverse osmosis removal efficiency is reported to be 95 % for As (V) (Government of Newfoundland and Labrador, 2006).

Table 1.1 Efficiencies and Prices (where available) for various Arsenic removal techniques

Technique	Arsenic removal Efficiency (Government of Newfoundland and Labrador, 2006)	Cost	Reference for costs of techniques
Activated alumina (AA)	51 %	$ 1200-1600 for low contamination levels (6-10 gpm)	Arsenic removal system, 2008
Granular activated carbon (GAC)	96%	$ 550 for a drum and it should be replaced every 9 to 12 month	Omitha Devendra, Customer service representative, Carbon Activated Corp, California, personal communication, 2008
Iron oxide coated sand (IOCS)	96%		
Ion exchange resins	40-90 %		
Nanofiltration	95 %	$ 14, 950 including a storage tank (1500 gpd)	RE Consumables Nanofiltration, 2008
Reverse osmosis	95 %	$ 13,975 including a storage tank (1000 gpd)	RE Consumables Reverse Osmosis, 2008

1.2.3 Selected Mechanism and Material

Membrane processes, ion exchange, coagulation, and solvent extraction have been used for metal and toxic elements removal; however, adsorption has been proven to be economic and cost effective for metal removal. Activated carbon is the most efficient and attractive adsorbent that has been used for effluent treatment, yet it is expensive (Poots and McKay, 1978). As a cheap alternative, agriculture wastes, wood and peat are also used after activation as sources of carbon. They can either be treated physically at high temperature to get rid of the volatile organic carbon (VOC) and chemically with acids (Cox et al., 2000; Poots and McKay, 1978). In this study, adsorption will be the technique used for arsenic removal and horticultural peat will be the substrate used for adsorption.

Sorption onto substrate surfaces is one of the most successful techniques in removing metals especially from aqueous solution (Budinova et al., 2006). Peat is defined as a "fibrous mass of organic matter in various stages of decomposition, generally dark in color, and of spongy consistency and as unconsolidated, hydrophilic carbonaceous sediment formed by the accumulation of partially fragented, decomposed and commonly heterogeneous plant remains which retain more than 75 % inherent moisture and less than 12 % mineral matter in saturated natural deposits" (Viraraghavan and Kapoor, 1995). Peat consists mainly of cellulose and lignin, which contain polar functional groups such as aldehydes, ketones, phenolic hydroxides, and ethers that contribute to the high cation exchange capacity (CEC) (Viraraghavan and Kapoor, 1995). CEC is the total of exchangeable cations that a material can adsorb at a specific pH. CEC is the product of the specific surface area (SSA) and surface charge density and its unit is either cmol/Kg

or mequ/100g. SSA is the ratio of the total surface area of a soil to its mass (Mitchell, 1993). Metal concentration in peat varies according to its type and its surrounding conditions. For the peat used in this study, Fe was the metal with the highest concentration (1060 mg/kg). Some metals were below the detection limit such as cobalt and chromium. The detecTable metals (Mn, Ni, Cu, Zn, Br, and Pb) ranged between 0.4 and 106.7 mg/kg (see Table A.11, p 130).

The use of peat as a source of carbon is a very attractive alternative for the removal of dissolved and suspended metals from drinking water, storm water, and diluted industrial waste stream due to two reasons. Peat is characterized by high polarity that enables it to sorb metals and polar organics, phosphorus, and potassium. Moreover, the availability of peat in North America, especially Newfoundland, makes it an attractive material (Brown et al., 1999).

1.3 Objective

The Objective of this study is to use a cheap and locally available substrate or adsorbent for reducing the Arsenic concentration in water below the accepTable level according to U.S.EPA and Canadian Environmental Quality Guidelines of 10 µg/l. Peat has a low point of zero charge (PZC) or isoelectric point that lies in the pH range of 2.5-3 below which the peat surface net charge is positive (Ringqvist and Oborn, 2002). On the other hand, the best pH range for Arsenic adsorption lies between pH 3 to 5 (Lorenzen et al., 1995). Morever, Arsenic does not react with functional groups, unlike metals that can

react with carboxylic, phenolic and other humic substances, which are the main constituents of peat (Viraraghavan and Kapoor, 1995), forming inner sphere complexes (Gu et al., 2005). Accordingly, for increasing the percentage removal of Arsenic from groundwater, peat can be used after being impregnated with Fe as an adsorbent. Fe can adsorb Arsenic especially after being oxidized to iron oxyhydroxide (FeOOH) by replacing the OH^- with Arsenic. Oxidation is also helpful as Fe^{3+} forms stronger bonds with functional groups than Fe^{2+} (Gu et al., 2005), Oxygen can be supplied to the metal solution to help in oxidation of Fe and to increase the quantity impregnated using a strong oxidizer.

Impregnation helps make use of the functional groups in the Arsenic removal process as the impregnated iron oxyhydroxide (FeOOH) on the surface of such groups can dissociate the OH^- group and adsorb Arsenic to form an inner sphere complex (Subramaniam et al., 1997). In addition, impregnation is expected to raise the PZC of peat since it has been used to increase the PZC of activated carbon (Reed et al., 2000). The most common species existing in water sources in Newfoundland is arsenate (Government of Newfoundland and Labrador, 2006), and the average pH of these sources is 7.2 (Guzzwell, 2006). This is why all the solutions prepared for testing Arsenic removal in this study are As (V) solutions.

1.4 General outline

The thesis consists of five chapters. The first chapter includes general information about Arsenic. It also introduces the Arsenic problem in Newfoundland and the methods,

software and materials that were used to study this problem. The second chapter summarizes the previous studies conducted in this area and their relation to this research. Chapter three discusses the methods, materials, tools and equipment that were used in this study. Chapter four shows the results and efficiency of the impregnated peats using column and batch studies. It also shows the results of the statistical analysis for the data obtained from the government of Newfoundland and Labrador and the results of characterization tests which were conducted to gather more information about peat such as zero point of charge, cation exchange capacity and acid digestion and how these characteristics affect the adsorption capacity of peat. The government data includes chemical and physical analysis for different wells in the province excluding Labrador, where the population is only about 30,000 (Wikitravel, 2008; Guzzwell, personal communication, 2006) and where Arsenic in drinking water has not been found to be a problem (Guzzwell, personal communication, 2006). The last chapter presents the conclusion and recommendation for future research to add to this research.

Chapter Two

Theoretical background

2.1 Arsenic and Metal Removal

Mercury (Hg), cadmium (Cd), zinc (Zn), copper (Cu), iron (Fe), nickel (Ni), chromium (Cr), silver (Ag), lead (Pb), arsenic (As) and antimony (Sb) are successfully attracted onto peat surfaces. This is because of the polar functional groups in peat such as aldehydes, ketones, acids, and phenolic groups, which are involved in chemical bonding and are responsible for the high CEC of peat (Ho et al., 2000). The carboxylic, phenolic and hydroxyl groups in fulvic acid (yellow water soluble active acid), humic acid (results from decomposition of lignin) and humin, which are attached to peat, are capable of dissociating hydrogen ions (H^+) (see Table 2.1) (Puustjarvi et al., 1980). In general, proton association and proton dissociation are the controlling factors of charge

inducement (Evans, 1989). When a charged ion is adsorbed to a surface, it either displaces another ion of similar charge such as the H^+ or another weakly attracted cation (ion exchange) or it is associated with another counter charge ion to maintain surface neutrality (co-adsorption) (Bowden et al., 1980).

Table 2.1 Functional groups in fulvic and humic acid (Snoeyink et al., 1980, p233)
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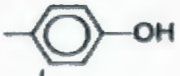
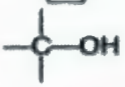
Property	Humic Acids	Fulvic Acids
Elemental Composition (% by weight)		
C	50–60	40–50
H	4–6	4–6
O	30–35	44–50
N	2–4	<1–3
S	1–2	0–2
Solubility in strong acid (pH 1)	Not soluble	Soluble
Molecular weight range	Few 100 → several million	180–10,000
Functional group distribution	Percent of oxygen in indicated functional group	
carboxyl —COOH	14–45	58–65
phenol 	10–38	9–19
alcohol 	13–15	11–16
carbonyl 	4–23	4–11
methoxyl 	1–5	1–2

Metals form two different kinds of complexes with peat or soil surfaces. They are outer sphere complexes also known as ion pairing or ion exchange, and strong inner sphere complexes (Evans, 1989). The former is a weak electrostatic association of hydrated cations with complexant ligands, while the later is a strong association between metals and complexant ligands by a covalent bond. The inner sphere complex is formed on

oxide and hydroxide surfaces and it includes the formation of covalent bonds, which prevent the dissociation or exchange of the adsorbed ion (Evans, 1989). An inner sphere complex is also formed between metals and functional groups of humic matter, which behave as complexant organic ligands. When there is more than one donor atom (O, N, and S) within the functional group, chelation occurs, which can be defined as multi-ligand complexation (Evans, 1989).

The formation of an inner sphere complex is pH dependent and the maximum adsorption occurs at a pH value close to the pK_a value of the adsorbate. "pK_a is equivalent to – log K_a which is the equilibrium constant for an acid that refers to the reaction in which the acid donates a proton to a water molecule…large values of K_a indicate that the acid has a strong tendency to donate a proton to water, i.e. it is a strong acid"(Snoeyink et al., 1980, p88). An acid might dissociate more than one proton; accordingly it might have two or more pK_a (pK_{a1}, pK_{a2}, ...) values. Acids that can donate one proton are called monoprotic acids (Butler and Cogley, 1998).

Outer sphere complexation, which is commonly known as ion exchange or non-specific adsorption, is formed due to the attraction between a negatively charged soil surface and cations in solution by electrostatic or coulombic forces. This force is weak and allows for further ion exchange in the future. Cation exchange is described in terms of the double diffused layer (DDL) (Evans, 1989). The DDL is a layer of cations formed at a distance from the soil surface due to two counter forces. According to Coloumbs law, cations will be attracted to negatively charged soil particles by electrostatic forces, however, cations

will tend to diffuse away from soil, according to Fick's law, to establish a uniform ion concentration throughout the soil solution (Bohn et al., 1985).

2.2 Arsenic Speciation and Adsorption

Arsenic commonly exists in aqueous solution as Arsenate (As V), which is stable in a moderately acidic medium, and Arsenite (As III), which is stable in a moderately alkaline medium as seen in Table 2.2 (Lorenzen et al., 1995). Arsenic is adsorbed due to the formation of inner sphere complexes, especially on iron oxyhydroxides and oxide surfaces, and by ion exchange as well. The ability of soil to retain elements depends on the element or metal speciation, pH, and mineralogical composition and organic carbon content of soil (Evans, 1989).

Peat is an abundant and cheap material but there are limited studies on its use for arsenic removal. Both peat and activated carbon (AC) have very high organic contents. However, activated carbon (AC) has been the focus of many studies especially those concerned with removing Arsenic from aqueous solution (Poots and McKay, 1978).

Speciation and pH should be considered when developing adsorption theory involving electrostatic interactions (Bowden et al., 1980). The major forms of As (V) are $H_2AsO_4^-$ and $HAsO_4^{2-}$ which exist at pH ranges of 2.24-6.76 and 6.76-11.6 respectively (see Table 2.2). If the final pH, which is one of the controlling factors for adsorption efficiency, is lower than 6.76 pK_{a2} (the second dissociation factor of As (V), see Table 2.2), the adsorption capacity increases (Tanjore and Viraraghavan, 1995). The pK_a values of

H_3AsO_4 are 2.24, 6.67, and 11.6 as can be seen from Table 2.2, which indicates that a pH value less than 6.67 will lead to more adsorption on the AC surface (Tanjore and Viraraghavan 1995). This is because, when the pH approaches 7 the surface of AC starts gradually to get neutralized and at pH 9 or more the negative charges on the AC surface increase, repelling the attracted Arsenic anions (Budinova et al., 2006). A pH range of 3 to 5 is perfect for arsenate removal (Lorenzen et al., 1995). In another study, the effect of pH on As (V) removal by activated carbon was studied. The effect of pH increase was slight as long as it did not exceed a value of 5. However, efficiency decreased from 58 % to 51 % when pH increased from 5 to 8 at an initial dosage of 25 μg/l. However, at an initial pH of 9 the efficiency dropped to 2 % (Chuang et al., 2005).

For As (III) adsorption on AC, maximum adsorption occurred at pH 7.9 (see Table 2.2) after which a sharp decrease in the uptake occurred approaching pH 10. This behavior was discussed in terms of pK_a values. As (III) exists in the neutral form of H_3AsO_3 and its adsorption is not favored, yet dissociation of this neutral form starts as the pH becomes alkaline and increases as it approaches a pH of 9.2 which is the pK_{a1} (first dissociation factor, see Table 2.2). Before this range, the driving force bonding Arsenic to carbon is physical adsorption. When the pH exceeds 7, the dissociation process results in the formation of the negatively charged arsenite ion, which can be attracted to the positive AC surface. However, at pH 9 or more the negative charges on the AC surface increase resulting in the repulsion of the associated anions (see Table 2.2) (Budinova et al., 2006).

Table 2.2. As speciation in aqueous solution at different pH levels (Rageh et al., 2007).

References	Arsenic Oxidation States	Abundancy	Different ionic Forms		
			Neutral form	Univalent Form	Divalent Form
(Lorenzen et al., 1995)	- 3	Not common			
(Lorenzen et al., 1995)	0	Not common			
(Budinova et al., 2006, Manju et al., 1998, Mohan and Pittman, 2007)	3	Common in aqueous phase (Arsenite)	H_3AsO_3 exist at pH less than 7 and keep decreasing till reaching 9.2 (pK_{a1})	$H_2AsO_3^-$ start to exist at pH 7 and increase gradually till reaching its maximum at pH range of 9.2 (pK_{a1})-12.1 (pK_{a2})	$HAsO_3^{2-}$ start to exist at pH range of 12.1 (pK_{a2}) to 13.4 mixed with $H_2AsO_3^-$ (pK_{a3})
(Chuang et al., 2005)	5	Common in aqueous phase (Arsenate)	H_3AsO_4 exist at pH less than 2.24 (pK_{a1})	$H_2AsO_4^-$ exist at pH range of 2.24 (pK_{a1}) - 6.67 (pK_{a2})	$HAsO_4^{2-}$ exist at pH range of 6.76 (pK_{a2}) - 11.6 (pK_{a3})

The pH value affects also the charge induced on the substrate surface. At a pH higher than the point of zero charge (PZC) of an adsorbent, its surface gets charged with opposite charges to those ones below the pH of the PZC (pH_{PZC}). However, shifting from one charge to another does not happen suddenly. Opposite charges start to gradually neutralize the existing one with the increase of pH until the PZC is approached, then the opposite charges start to increase until they dominate and interfere with the adsorption process (Budinova et al., 2006). The effect of increasing the pH when approaching the PZC and slightly after exceeding it depends also on the type of ion adsorbed. For a non charging ion such as chloride, the activity of the solution remains constant yet the AC surface gets more negatively charged decreasing the adsorption. On the other hand, the adsorption of $H_3SiO_4^-$ increases with pH. This is because the activity of $H_3SiO_4^-$ significantly increases with pH (up to ten fold). Such an increase in activity overweighs the increase in electrostatic repulsion associated with the pH increase. This will happen as long as the pH is still below 9.5 and after that the electrostatic forces will be the dominating factor and the adsorption rate will start to drop. For cations, such a behaviour can not be observed because precipitation occurs at high pH values (Bowden et al., 1980).

Arsenate (As V), the oxidized form of arsenic in the aqueous phase, was chosen since it is the dominant species present in Newfoundland groundwater (Government of Newfoundland and Labrador, 2006). Moreover, As (V) is less soluble and less mobile than arsenite (As III), the reduced form. In previous studies, As (V) was removed in higher percentages than As III (Jiang, 2001). In addition, at low pH levels As III species

are present in non-ionic or neutral form (H_3AsO_3) and can not be efficiently attracted to charged surfaces (Mondal et al., 2007). Dissociation of this neutral form starts as the pH becomes alkaline and increases as it approaches a pH value of 9.2 (pK_{a1} = 9.2, see Table 2.2). When the pH exceeds 7, the dissociation process results in the formation of the negatively charged arsenite ion, which can be attracted to positive surfaces (Budinova et al., 2006).

The PZC also known as isoelectric point of peat is low. According to Ringqvist and Oborn (2002), it lies in the pH range of 2.5-3 below which the peat surface charge is mostly positive. Even after impregnation the range is not expected to increase by more than 1.2 pH units (Reed et al., 2000; Tschapek et al., 1974). Accordingly, As (III) cannot be removed by peat at such a low pH value since it is neutral. Increasing the pH will not help due to the repulsive forces induced by high pH on the surface of peat that becomes more negatively charged with pH increase, decreasing the affinity of peat towards As (III). On the other hand, the ionic forms of As (V) are $H_2AsO_4^-$ and $HAsO_4^{2-}$ existing at pH ranges of 2.24-6.76 and 6.76-11.6 respectively (See Table 2.2). If the pH of the system is above 2.24 (pK_{a1}), As (V) can be removed as it exists as an anion form at this pH level and the surface will be positive (Chuang et al., 2005).

2.3 Peat Characteristics

Peat is a polar material that can sorb organic matter, phosphorus, metals, and potassium. Peat has a high porosity (Brown et al., 1999), a low pH_{PZC} of 2.5 to 3 (Ringqvist and Oborn, 2002), a high CEC, and a high SSA. The following Table 2.3 summarizes findings of former studies of CEC and SSA for different types of peat including Horticultural peat, the peat used in this study.

Table 2.3 CEC and SSA of different kinds of peat

Type of peat	CEC (cmol/Kg)	SSA m^2 /g.	Reference
Herbaceous peat	97.1	200	(Brown et al., and Allen,1999)
Alfred peat (Ontario)	102.8		(Comerton et al., 2002)
Revere de loup (Quebec)	118		(Comerton et al., 2002)
St-Modeste (Quebec)	25.5		(Comerton et al., 2002)
Montverde peat (Palm beach)	155		(Jardine et al., 1985)
Horticultural peat	72.6	78.17	(Viraraghavan and Kapoor, 1995); (Tanjore and Viraraghavan 1995)
Sphagnum moss peat	246	200	(Abdel Warith, 1996)

In previous studies, peat was used for the development of organic matter for its commercial use as an adsorbent (Brown et al., 1999). Peat is defined as "young

quaternary, mainly Holocene, organogenic sedimentary rock in the first stage of coalification" Twardoska et al., 1999). It is abundant in North America and it is well known for its ability to remove metals from leachate and wastewater. The total peat available in the world is about 1000 billion tons (dry weight), 77% of which is available in Canada and U.S.A. while the rest is in Indonesia (6 %), Scandinavia (7%), and other different countries (10%) (Twardoska et al., 1999).

The main peat forming plants are sphagnum mosses, true mosses (Bryales), sedges and woody plants. Sphagnum mosses are made of cells having thin lignified walls with large cavities that can transport water even after the plants die. Lignified walls prevent the collapse of the plant and keep moisture and air content to a certain level. Stems and leaves of moss peat can absorb, store and then later release nutrients, a property that other plants acquire after becoming peat (Puustjarvi et al., 1980).

Peat consists of lignin, cellulose, hemi-cellulose, resins, fats, and water-soluble constituents. Parts of cellulose and hemi-cellulose decompose reducing their percentage while lignin and other constituents decompose forming humic acid. Humic acid causes peat to irreversibly dry out. However, the high carbon content of cellulose is decomposed by microorganisms, which increases the nitrogen content. The high content of humic acid causes the formation of clods and leaching of nitrogen. In winter clods expand and break down and by changing the season the peat structure becomes granular. Adding lime to humic acid converts it to calcium and magnesium humates, which are less water repellent and more granular (Puustjarvi et al., 1980).

Structurally peat can be divided into primary particles, secondary particles and amorphous mass. Primary particles are those particles formed due to breaking up of sedges, stems, roots and sphagnum moss by mechanical action. They range between 0.1 mm to a few centimeters in size. Amorphous substances are made of complex organic substance. Secondary substances include calcium humate and polysaccharide. Water occurs in peat due to capillary action, and hygroscopic and gravitational forces (Puustjarvi et al., 1980).

The chemical composition of peat does not include any of the essential nutrients required by plants. However, carboxylic groups, phenolic hydroxyl groups, fulvic acid, humic acid and humin, which are attached to peat, are capable of dissociating hydrogen ions (H^+) (see Figure 2.1) and attracting other ions instead. The higher the valence a cation has the stronger the bond it will have with peat (Chuang et al., 2005).

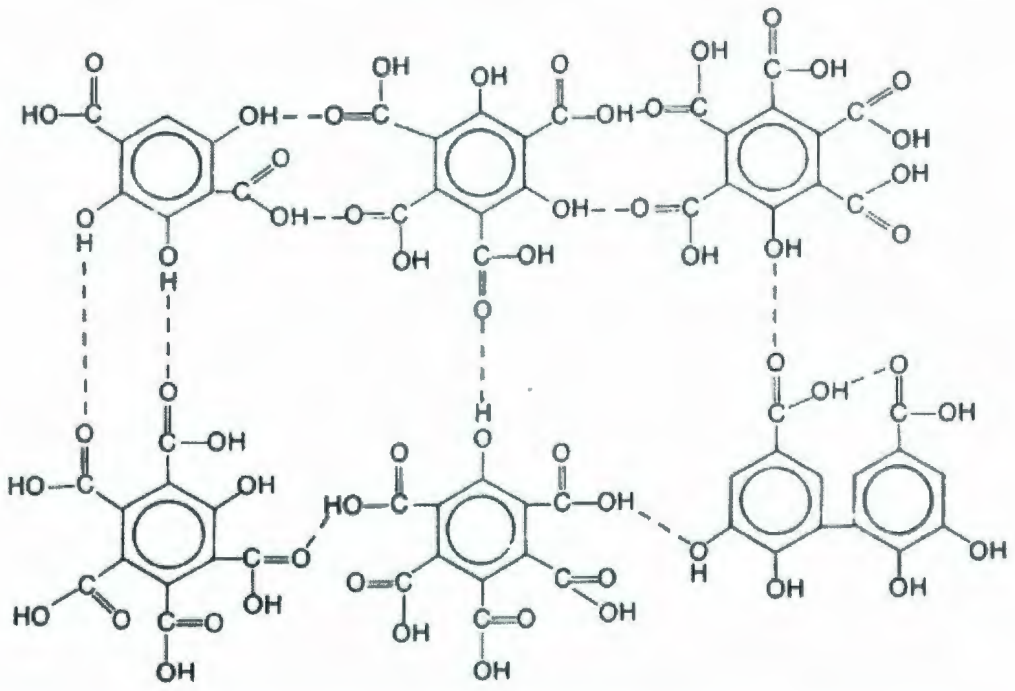


Figure 2.1. Suggested structure of fulvic acid (Snoeyink et al., 1980, p233)

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For different types of peat, both ash content and extent of decomposition are decreasing in the following order: gyttia > peat humus > rush peat > sedgeous peat > hypnum moss peat > sphagnum moss peat. The results of batch experiments in a previous study showed that less decomposed peat or low moor peat had a better sorption capacity for metals than highly decomposed peat or high moor peat in the following order: peat humus and rush peat > hypnum moss peat >sphagnum moss peat > gyttia. The extent of decomposition, ash content, and pH of the peat were not correlated with the decreasing order of the binding capacity (Twardoska et al., 1999). However, durability of peat was negatively correlated with the degree of humification (Abdel Warith, 1996). The horticultural peat as used in this study is a type of sphagnum moss peat (Viraraghavan and Kapoor, 1995).

The studies done on peat suggest that metal binding occurs mostly due to ion exchange. This is because an increase in the Ni concentration in a peat-Ni solution leads to the decrease in the pH, which indicates the release of H^+ ions and its replacement by the metal. Yet, there are other suggested reactions such as chemisorption, complexation, and adsorption-complexation. It is believed that metals react with the carboxylic and phenolic acids of the fulvic and humic acid that result from peat humification (Brown et al., 1999).

There are many different views and theories for adsorption and metal uptake that have been proved in previous studies. In a study on peat using a $Cu(NO_3)_2$ solution, a significant amount of NO_3^- was adsorbed causing the adsorption of more Cu, to neutralize the negative charge of NO_3^-, rather than ion exchange occurring. This kind of bonding is considered to be a combination of adsorption and complexation. Further, in another study, humic acid was extracted and it was able to form a chelating complex with Cu through its carboxylic group, yet the peat from which humic acid was extracted adsorbed more Cu after the humic acid was removed. This confirms that physical adsorption and complexation are the reasons for the Cu bonding (Brown et al., 1999).

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2.4 Peat Impregnation

In former studies, As (III) was removed by using a precipitation method with iron oxide coated sand, and red mud which are very efficient in retaining Arsenic (Budinova et al., 2006). However, due to the small particle size of oxides, it was difficult to use them in continuous flow systems. Therefore, they were combined with other adsorbents. Many

studies were conducted on mixing oxides with different materials such as sand and AC (Vaughan and Reed, 2005; Reed et al., 2000). The former has a very low surface area, which cannot allow for enough impregnation, unlike activated carbon.

The combination of AC and oxides resulted in a mix having a capacity for heavy metals that was more than that of iron oxide alone (Vaughan and Reed, 2005). Activated carbon was chosen due to its known high sorbing capacity, especially to Arsenic. In former studies, it was shown that As (III) adsorption by hematite was 2.63 μmole/g, while adsorption by sulfate modified iron oxide coated sand was 1.91μmole/g. Activated bauxite, activated alumina, iron hydroxide loaded coral lime stone and red mud showed adsorption capacities of 16, 14, 1.91, and 8.86 μmole/g respectively. Physically treated carbon showed the highest adsorption capacity of 18.6 μmole/g (Budinova et al., 2006).

According to previous studies impregnating carbon with metals helped improve adsorption. This was done by mixing carbon with a 0.001 M metal solution under alkaline conditions to enhance the formation of metal hydroxide precipitates, which can form insoluble metal arsenate removing more Arsenic from solution (Lorenzen et al., 1995).

The peat adsorption capacity as well was improved in the presence of oxides. When the peat deposit buried under the Vancouver city sanitary landfill was tested, it was found that heavy metals presence was associated with Fe and Mn and not with carbon or sulfur. Most of the heavy metals were sequestered in the lower layer of peat where iron from the

landfill percolating leachate was concentrated (Mathews and Bustin, 1994). Moreover, elements such as As, Pb, Al, and S can be retained by peat for a long time in the presence of Fe (Mathews and Bustin, 1994). This is because oxides of Fe as well as Mn are the best adsorbents of Arsenic (Evans 1989). In another study more Cu was adsorbed onto poorly humified carex peat than onto sphagnum peat. This was thought to be due to the fact that the Fe content of carex peat was higher (Ringqvist and Oborn, 2002).

There were many studies concerned with impregnating AC and carbon extracted from peat and agriculture wastes. Cu > Fe (III) > Fe (II) impregnation resulted in a very high removal efficiency of Arsenic in the above mentioned descending order (Lorenzen et al., 1995). In a study on agricultural wastes, it was found that 200 mg of Cu impregnated coconut husk carbon (CICHC) or 1000 mg of coconut husk carbon (CHC) was required for the removal of 50 mg of As/l, which indicated that impregnation improved CHC by 5 times (Manju et al., 1998). Therefore, Cu and Fe were chosen as the most efficient metals for AC pretreatment. The anion used with Cu was having an impact on the adsorption process. Chloride was found to be the best anion and cuprous chloride was the best salt and this is why chloride was chosen to be the anion used in this study(Lorenzen et al., 1995).

2.5 Factors Affecting Arsenic Retention by Activated Carbon

In addition to the formation of the insoluble metal arsenate mentioned, there is another mechanism involved in adsorption of Arsenic. The formation of an outer sphere complex can be proved by the results of a former study in which AC was used for the removal of As (III). The uptake rate increased sharply in the beginning, then gradually when approaching equilibrium after 60 min. Accordingly, it was believed that the controlling mechanism of removal was based on the formation of monolayer coverage of As (III) on the surface (Budinova et al., 2006).

For AC and peat-based carbon, the majority of adsorption occurs at the surface due to ion exchange. On the other hand, in Fe impregnated carbon the Fe hydroxide and/or oxyhydroxide are the ones responsible for ligand exchange and inner sphere complex formation. As (V) exists in four different species. At typical pH (4-10) only two species can occur, $H_2AsO_4^-$ and $HAsO_4^{-2}$. For ligand exchange, these two species will exchange OH^- attached to Fe. $H_2AsO_4^-$ will be the species exchanged at pH < 7, while $HAsO_4^{-2}$ will be exchanged at pH > 7 (as shown in Table 2.2, page 20). In general, the adsorption of As onto GAC alone was very small compared to iron impregnated activated carbon (FeAC) (Vaughan and Reed, 2005). Figures 2.2, 2.3, 2.4 and 2.5 show successively the impregnation of carboxylic and phenolic functional groups followed by As (V) adsorption. For As (III) when the pH approaches 8.5 until reaching 9.2, $H_2AsO_3^-$ starts to replace the neutral form and As (III) becomes negatively charged as illustrated in Table 2.4 below

Table 2.4 The effect of pH on the peat charge and As and Fe uptake. (adapted from Ringqvist and Oborn, 2002; Chuang et al., 2005; Budinova et al., 2006; Manju et al., 1998; Henrot and Wieder, 1990; Gu et al., 2005; Brown et al., 1999).

pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Peat Charge	+ ve		Mostly + ve	Mostly – ve		- ve								
As(V) valence	Neutral			-1				-2					No available Literature	
As(III) Valence	Neutral						-1				-1 & -2		No available Literature	
As (V) uptake	Very Low (neutral)		The highest			Still high until it becomes a factor of the surface charge of adsorbent							No available Literature	
As (III) uptake	Very low (neutral)							Increases with pH until the uptake becomes a factor of surface charge of the adsorbent						
Fe Uptake	Very low since peat surface is +ve		Low	Very high		High		The governing mechanism will be precipitation						

The surface of FeAC is positively charged below a pH similar to PZC yet the Arsenic species is neutral. Above the PZC the surface of FeAC becomes negatively charged which will create counter repulsive forces reducing Arsenic adsorption with the increase of pH. Functional groups do not form complexes with metal anions and most of the adsorption is attributed to physical adsorption (Reed et al., 2000). This is because functional groups cannot exchange OH^- and they can only dissociate H^+ since organic oxygen present in such groups has different characteristics than the molecular oxygen (see Figure 2.2) (Puustjarvi et al., 1980). Moreover, organic oxygen has a very low

contribution to the oxidation process as well (Henrot and Wieder, 1990). Some of the functional groups do not form metal complexes. The alcoholic group, for example, does not react with metals despite having an OH^- group (Snoeyink et al.,1980; Viraraghavan and Dronamraju, 1993).

It has been reported that after impregnation the SSA and pore volume of carbon or activated carbon decreased yet the Fe content increased from 0.62 to 7 %. The pH_{PZC} increased from 7.5 to 8.2-8.7. For anionic As (V), the removal decreased with pH increase and vice versa for Hg and Pb. However, As(III) removal was not pH dependent at pH below 5. Above this value, the removal of As(III) increased until reaching a neutral pH, then the adsorption decreased with pH increase. According to former studies, As (V) and As(III) form inner sphere complexes with iron oxides. Moreover, the charged surface of FeAC helps in attracting counter ions and the formation of the double defused layer (DDL) (Reed et al., 2000). The following four diagrams show the impregnation of carboxylic and phenolic groups with Fe followed by Arsenic adsorption.

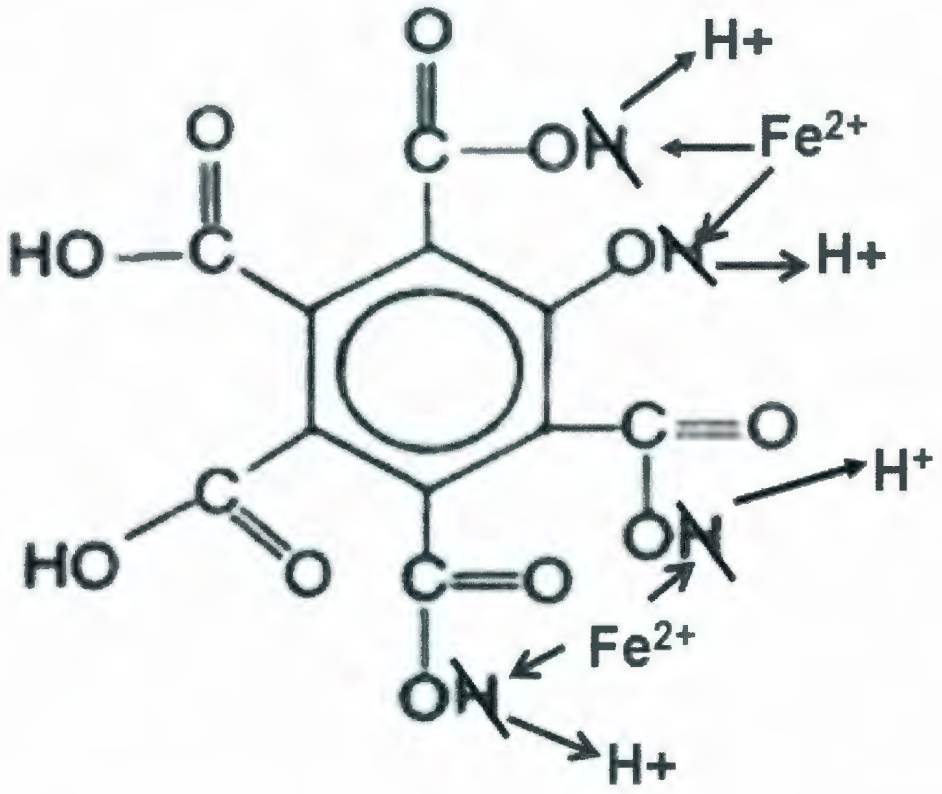

Figure 2.2 Carboxylic and phenolic groups impregnation with iron:

Carboxylic and phenolic groups can dissociate two protons and adsorb Fe^{2+} instead (Snoeyink et al.,1980).

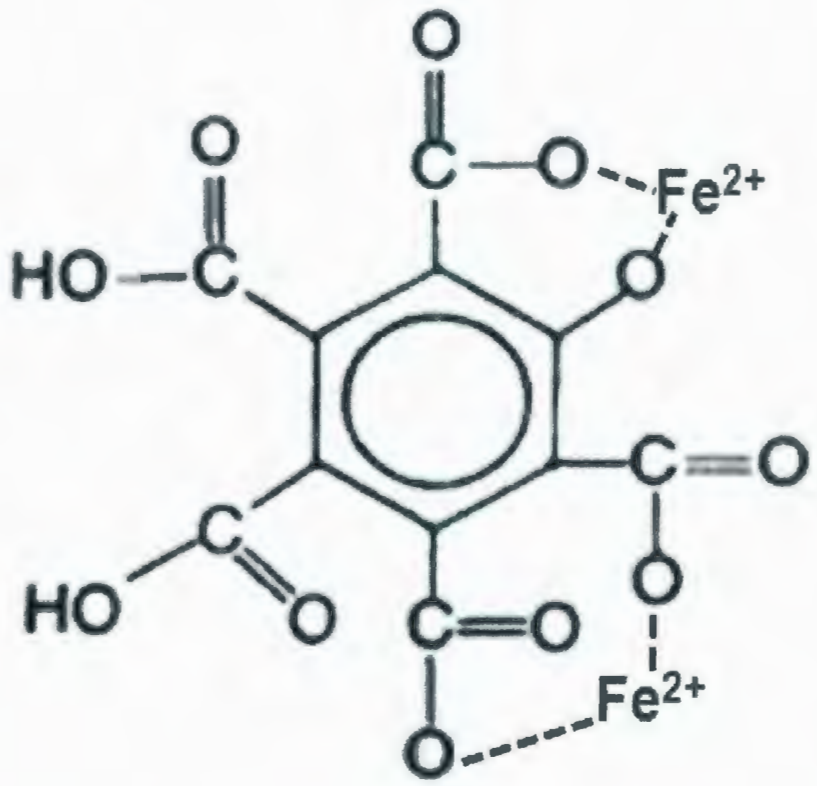

Figure 2.3 Fe^{2+} replacing H^{+}:

Fe^{2+} replaces H^{+} forming week bond with carboxylic and phenolic groups

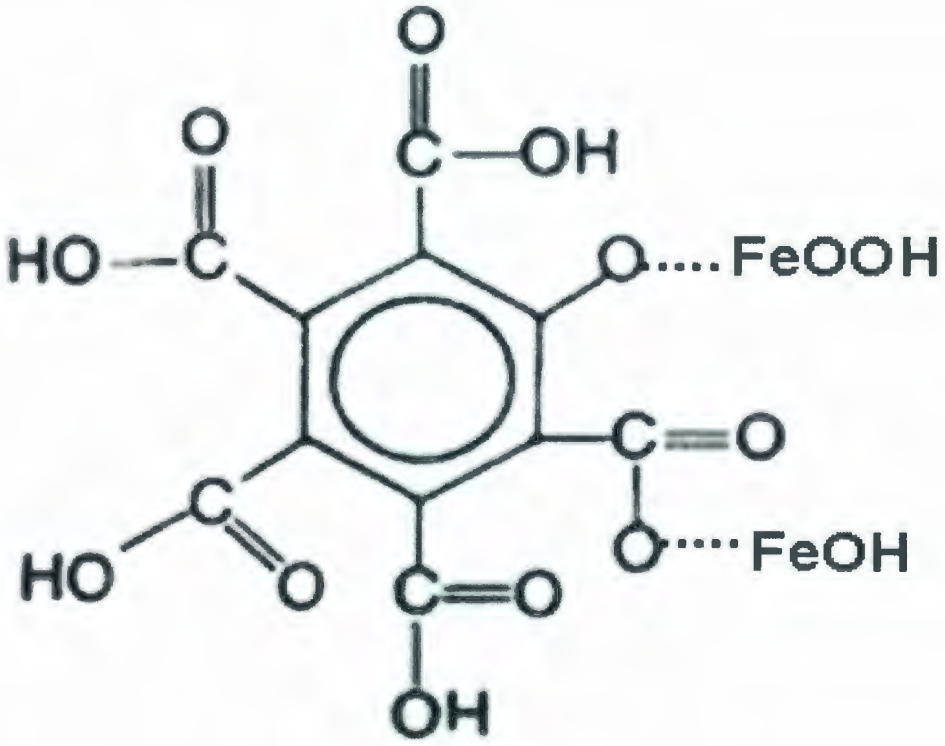

Figure 2.4 Oxidation of Fe^{2+} to Fe^{3+}:

An oxidizer can be added to oxidize Fe^{2+} to Fe^{3+} which can be further oxidized to an oxyhydroxide or a hydroxide form. Moreover, Fe^{3+} forms stronger bonds with functional groups more than Fe^{2+} (Gu et al., 2005).

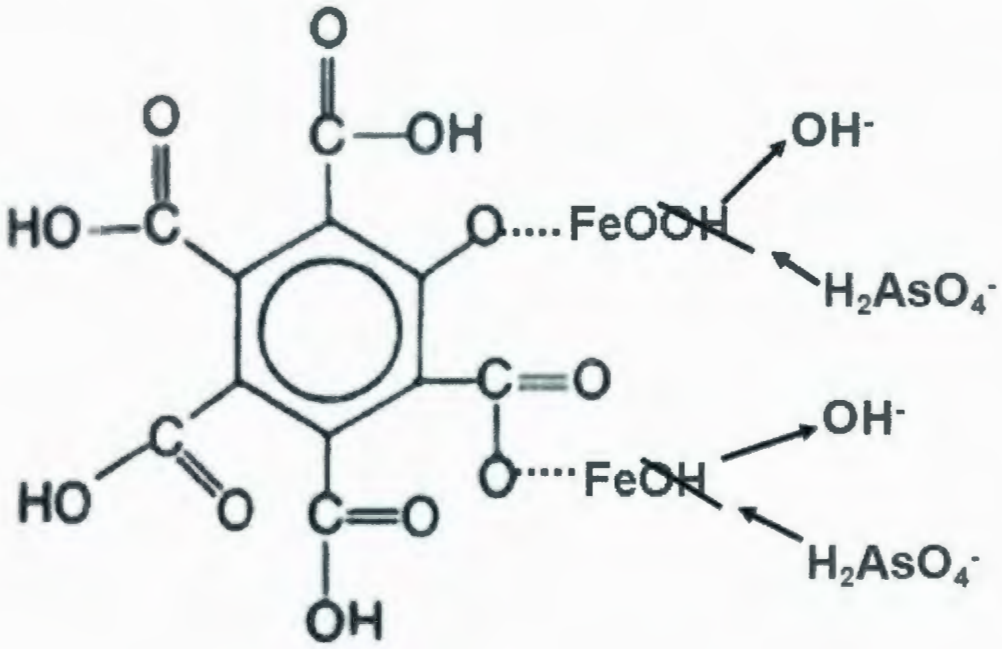

Figure 2.5 Adsorption of Arsenic:

Arsenic can be adsorbed onto the iron hydroxide surface releasing OH^- into the solution. The mechanism of adsorption in this case is inner sphere complexation. In this way, the high organic content of peat can be taken advantage of in the Arsenic removal process.

In a former study, Cu was used for impregnating AC for the removal of As (III). The change in pH from 3 to 12 increased the Arsenic removal from 16 to 88.6 % and from 10 to 83% for concentrations of 50 and 100 mg/l respectively. The maximum uptake was reached at pH 12 at which point the two main existing species of As were $H_2AsO_3^-$ and $HAsO_3^{2-}$. A chemical reaction (inner sphere complexation) as well as the formation of a low solubility precipitate $CuHAsO_3$ were the controlling uptake mechanisms (Manju et al., 1998).

2.6 Factors Affecting Impregnation Efficiency

The volume and concentration of Fe in a peat-Fe solution control the quantity of Fe impregnated. Organically bound Fe and exchangeable Fe on a peat surface represented 42% and 43% of the total Fe in peat respectively. In a previous study, when peat was exposed to an acid mine drainage solution with high Fe concentration, organically bound Fe increased by 4 folds reaching a saturation level of 12 mg Fe/g peat (finite process). The iron oxide concentration in peat kept increasing though with exposure to more volumes of iron solutions. The mechanism responsible for iron oxide retention after the organic sites became saturated was precipitation. Iron oxide kept accumulating on peat reaching a concentration of 99 mg Fe/g of dry peat. Precipitation of Fe oxides requires oxygen availability since organic oxygen attached to functional groups has a very little contribution in the oxidation process unlike molecular oxygen, which can be supplied to solutions through bubbling or by introducing an oxidizer to the system (Henrot and Wieder, 1990).

In another study about adsorption of Fe onto peat, it was shown that sources of oxygen can be biotic or abiotic. At pH 3.5 the later mechanism was not efficient yet the former was the controlling mechanism of oxidation. This was proved by adding antiseptic, which inhibited the oxidation at low pH. However, at pH above 5 the auto-oxidation, by oxygen present in the Fe solution, was the governing process and adding antiseptic did not have much influence on the oxidation process. High concentrations of Fe had a negative effect

on Fe oxidation. 100 mg/l Fe was the optimum concentration at which the best efficiency of Fe removal was obtained (Henrot and Wieder, 1990)

Oxygen availability in solution is one of the important factors for organic substances adsorption as well. For granular activated carbon (GAC), the increase of molecular oxygen in solution increased the adsorption capacity for organic matter due to polymerization of organics agitated by the carbon surface. The increase in dissolved oxygen (DO) concentration from 10 to 26 mg/l increased the adsorptive capacity of pentachlorophenol by 2.7 times (Tanjore and Viraraghavan, 1995).

Former studies showed that the organic content of the substrate played a great role in impregnation. Organic matter's ability to uptake Fe is attributed to the oxygen-containing functional groups such as carboxyl, carbonyl, hydroxyl, phenol, and enol groups. In a previous study, it was shown that carboxylates had the ability to complex metals. Humic and organic substances can act as a sink for metal ions as well as means for their transport and mobility. Humic substance consists of humin, fulvic acid and humic acid (Gardea-Torresdey et al., 1996). Impregnation decreases the SSA of soil, however, it has been documented that the SSA has no effect on Arsenic adsorption and no correlation was found between these two variables (Lorenzen et al., 1995; Budinova et al., 2006). Adsorption of organic compounds such as BTEX is attributed to the high CEC, high organic carbon content, and SSA of adsorbent but adsorption of Arsenic is not (Comerton et al., 2002).

2.7 Precipitation, Dissolution, and Desorption

Precipitation and dissolution can be described in terms of the solubility product and activity product (Evans, 1989). "The solubility product is the colloquial term for the equilibrium constant that describes the reaction by which a precipitate dissolves in water to form its constituent ions" (Snoeyink et al., 1980, p249). If the concentration of ions or ion activity exceeds the solubility product, hydrolyzed oxides and hydroxides are precipitated. All metals can be hydrolyzed except alkali and alkaline earth metals. The rate of precipitation increases with increasing the pH (Evans, 1989). Adding HCl or NaOH to have extremely acidic or extremely alkaline conditions results in desorption. However, the acidic condition results in desorption of impregnated metals as well, which is not the case at pH above 10 (alkaline condition) since the metal gets retained in the form of metal hydroxides (Manju et al., 1998).

2.8 Minitab

Minitab is a software package for statistical analysis of simple and complex functions (Zehna, 1992). Minitab was used in this study to statistically analyze the data obtained from the government of Newfoundland and Labrador for the contaminated sources. Two different analyses were done using Minitab to determine the possible reasons and factors contributing to the presence of Arsenic at high concentrations. The first was a correlation analysis between Arsenic and all detected elements present in water samples as well as some chemical and physical properties. The correlation analysis was also done for the

data obtained from the analysis of treated water from both batch and column tests using ICP-MS. The second was a principal component analysis or a multivariate analysis used to transform correlated variables into a smaller set of uncorrelated ones and it was only done for the data obtained from the provincial government (Jackson, 2003).

The significance of the parameters analyzed by Minitab was decided according to Table 2.5, which consists of four columns. The first column is for the degree of freedom (df), which is a value equivalent to the number of samples minus two. The second, third and forth columns are for the corresponding significant absolute values of correlations or Pearson's correlations (r) at three different p-values which are 0.1, 0.05, and 0.01 (Rageh et al., 2007). The p-value is the probability of error when considering a significant correlation. In Table 2.5, it can be noticed that the higher the degree of freedom the lower the value of correlation accepted. The sign of a correlation reflects the proportionality of the relation between Arsenic and the other parameter while the value of correlation represents the strength of relation (Vincent, 1995; Rageh et al., 2007).

Table 2.5 Pearson's Correlation (adapted from Vincent, 1995).

	P-value Pearson's correlation		
df	0.10	0.05	0.01
14	0.426	0.497	0.623
15	0.412	0.482	0.606
16	0.400	0.468	0.59
17	0.389	0.456	0.575
18	0.378	0.444	0.561
19	0.369	0.433	0.549
20	0.360	0.423	0.537
25	0.323	0.381	0.487
30	0.296	0.349	0.449
40	0.257	0.304	0.393
50	0.231	0.273	0.354
60	0.211	0.250	0.325
70	0.195	0.232	0.302
80	0.183	0.217	0.283
90	0.173	0.205	0.267

2.9 Detecting Arsenic Levels

The cost of analyzing an arsenic sample in commercial laboratories ranges from $15 to $50. Such laboratories use EPA approved methods and equipment such as graphite furnace atomic adsorption (GFAA), inductively coupled plasma mass spectroscopy (ICP-MS), or inductively coupled plasma emission spectroscopy (ICP-ES). Using Arsenic test

kits is a more economical alternative that can be used for detecting Arsenic levels. Spear et al. (2006) conducted a study for evaluating 7 different commercially available Arsenic kits based on accuracy, precision, ease of use, and matrix effect or competitive effect of other elements such as sulfides and antimony that have similar chemical properties as arsenic.

Samples having different concentrations of As (V) and As (III) solutions, of ratio 1:1, were measured using the seven kits and the results were compared to those measured by GFAA. Different replicates of each concentration were used to measure accuracy and precision. The cost for analyzing a sample using kits ranged from $ 0.30 to 4.40. Two of the kits that were suggested by the authors of this paper for testing Arsenic concentrations less than 100 μg/l were the La Motte and Quick II. Their minimum limits of detection are 4 μg/l and 1 μg/l respectively. They were the most accurate and expensive kits. The cost per test using La Motte and Quick II were $3.06 and $4.40 respectively while the test time for both of them was 16 min (Spears et al., 2006).

For this study, the La Motte kit was preferred as competitive elements had a minimum effect on the Arsenic concentrations obtained using this kit. Moreover, it could detect a wider range of Arsenic levels, though the lowest detection level of arsenic is < 4 μg/l. The range that can be detected by La Motte is from <4 to >500 μg/l. On the other hand the range that can be detected by Quick II is 1 to > 100 μg/l, however, the presence of competitive elements in water such as antimony might negatively affected the recovery of arsenic when using Quick II (Spears et al., 2006). Although the concentration of

antimony in groundwater in Newfoundland ranges between 0.5 to 3 µg/l, which is not high, it might interfere with the recovery of Arsenic if groundwater is tested using Quick II (Guzzwell, 2006).

Chapter Three

Materials, Methods, Tools and Equipment

The material used in this study for adsorption was horticultural peat impregnated with $FeCl_2$. In order to oxidize Fe^{2+} to Fe^{3+}, which forms stronger bonds with organic substances, sodium hypochlorite was used. The arsenic species used for preparing the Arsenic solution was As(V).

The aim of this study is to load peat with the optimum amount of iron to react with the associated phenolic and carboxylic groups for improving the adsorption capacity of peat. Functional groups do not react with Arsenic, though, it can react with iron hydroxides and oxyhydroxide (FeOOH), which are able to form complexes with Arsenic. The

optimum iron solution concentration used to impregnate activated carbon was found to be 2.34 to 2.5% (Gu et al., 2005).

It has been reported that the increase in the Fe/As ratio increases the Arsenic uptake. However, when the percentage of impregnated Fe exceeds a certain level, the inner pores get filled with oxyhydroxides reducing the surface area, blocking the pores, and decreasing Arsenic uptake. However, in other studies it was shown that the SSA had no effect on Arsenic adsorption and no correlation was found between these two variables (Lorenzen et al., 1995; Budinova et al., 2006). The optimum reported iron content in activated carbon was 6% by weight (Gu et al., 2005).

3.1 Materials

3.1.1 Iron

For impregnation, ferrous chloride ($FeCl_2$), the reduced form of iron (Fe^{2+}), was used since it is more soluble than ferric chloride ($FeCl_3$). This enables Fe to defuse more to inner pores of peat and react with functional groups. At pH ranging between 4.5-5, Fe^{2+} is soluble which will increase its mobility and capability to diffuse. Fe^{2+} forms weak bonds with functional groups (carboxylic and phenolic groups) which can be strengthened by oxidizing Fe^{2+}, after its diffusion, to Fe^{3+} that forms stronger complexes with ligands. Fe^{3+} can be easily hydrolyzed, at a pH higher than 3, to iron oxyhydroxide which has a strong affinity for arsenate (Gu et al., 2005; Brown et al., 1999). Iron (II) chloride tetra

hydrate 99 + % with 10 μg/g arsenic content from Fisher Scientific was used for this research. The arsenic content of the iron chloride contributed to the release of arsenic from iron impregnated peat to the arsenic solution to be treated during batch and column tests.

3.1.2 Oxidizer

Using an oxidant is important in the impregnation process as it increases the amount of Fe adsorbed to more than double when compared to bubbling oxygen alone. Sodium hypochlorite has been proven to be the best oxidizer for impregnation and arsenate removal (Gu et al., 2005). It is also cheaper than other oxidizers such as potassium permanganate and hydrogen peroxide. In this study, sodium hypochlorite from A&C Chemicals, 9-12 % solution and active chloride of 5.68 %, was used. Sodium hypochlorite reacts with acids producing poisonous gas that's why all pH adjustment were carried out in the fume diffuser.

3.1.3 Acids and Bases

H_2SO_4 was avoided for reducing the pH level. According to some studies, sulfates compete with Arsenic on adsorption sites (Katsoyiannis and Katsoyiannis, 2006; Jiang, 2001). For controlling the pH level, HCl and NaOH, from A&C Chemicals, were used in this research. During the column tests, the optimum pH level at which the Arsenic level in the effluent dropped below the 10 μg/l allowable limit was found to be 4.3.

3.1.4 Arsenic

Arsenate (As V) was chosen since it is the dominant species present in Newfoundland Groundwater (Government of Newfoundland and Labrador, 2006). As (V) is also less soluble and less mobile then As (III). As (V) oxide, 99.9 + % from Acros Organics, was used.

3.2 Characterization Tests

3.2.1 Point of Zero Charges Measurement (PZC)

There are different methods for determineng the PZC such as the electrophoretic mobility, the change of pH by adding adsorbent to solution (addition method) and the titration method. Electrophoretic mobility is the ratio of the migration rate of ions to the intensity of their surrounding electric field. This mobility is proportional to the charge of the ions. However, neutral particles show electrophoretic activities as well, which is the drawback of this method (Knecht et al., 2007). In the addition method, the PZC of a material is determined by measuring the change of pH when adding 1g of the material to a certain volume of water solution of KCl with predetermined ionic strength and pH. At PZC there should be no change in pH. However, the value obtained for the PZC varies

according to the concentration of the supporting electrolyte (KCl) which makes the applicability of this method questionable (Tschapek et al., 1974).

Titration with acid and alkali was used in this study as it was shown to be a reliable method by previous studies (Tschapek et al., 1974). In this method, the change in pH against the change in surface charges is recorded and plotted for soil suspensions in solutions of different ionic strengths of supporting electrolyte as KCl or NaCl (Coles and Yong, 2001). The intersection of plotted lines corresponds to the PZC. The different lines are obtained by adding 2 or 3 g of soil to 20 to 30 ml of different concentrations of NaCl or KCl to which certain volumes of acid or base are added at fixed time intervals while recording the change in pH (Tschapek et al., 1974; Coles and Yong, 2001).

Procedure followed for obtaining the PZC

1- Four solutions of NaCl, which is the supporting electrolyte, of concentrations 1, 0.1, 0.01, and 0.001 M were prepared.
2- 2 g of peat were added to 30 ml of each NaCl solution and duplicate solutions.
3- The eight samples were left to mix for more than one hour on a magnetic stirrer
4- One of the duplicate samples was treated with 0.1 N HCl while the other duplicate sample was treated with 0.01 N NaOH .
5- After adding HCl or NaOH, the pH reading was taken every 5, 7, 10 ,12, 15, 17 and 20 minutes to determine the proper interval of time before adding more base or acid which was found to be 15 minutes.

6- The titration experiment was conducted by adding 2 ml of 0.1 N of HCl or 4ml of 0.01 N NaOH every 15 min.

7- The peat suspension and solutions were placed on a magnetic stirrer to insure proper mixing of the suspension, solution and acid or base.

8- The pH was recorded every 15 minutes.

9- The cumulative amount of acid (H^+) or base (OH^-) added was represented in mequ/ g and was plotted against the change in pH..

The same procedure was followed for the impregnated soil, but the normality and volume of solution differed. 0.5 ml of 0.1N HCl solution and 1 ml of 0.1 N NaOH were added every 15 minutes for the acid and base titration respectively of the soil impregnated with 1.08 M Fe. For soil impregnated with 0.54 M Fe, 1 ml of 0.1N HCl solution and 1 ml of 0.1 N NaOH were used. For peat samples impregnated with 0.01 and 0.054 M Fe, 1 ml of 0.1N HCl solution and 2 ml of 0.1 N NaOH were used.

3.2.2 Cation Exchange Capacity Measurement (CEC)

The CEC was measured in this research using analytical method 82-006 "CEC at pH 7.0 by $Ca(OAc)_2 - CaCl_2$" (Sheldrick, 1984). All the solutions used and prepared had the same concentrations, molarity and normality as described in the method but the quantities were reduced to one third. This is because the centrifuge available had only 30 ml centrifuge tubes. For example 1 g of soil was used instead of 3 g and 13.33 ml of NaCl was used instead of 40 ml. Triplicates of the untreated peat and each of the impregnated

soil samples were tested and an Atomic Adsorption spectrometer (AAS) was used to detect the final calcium concentration. The model for AAS was a Varian SPECTRAA 55B.

3.2.3 Acid Digestion

Method 3050B "acid digestion of sediments, sludge and soils" was followed in this study for acid digestion of horticultural peat (U.S.EPA, 1996) to detect Fe and Arsenic content of the untreated and impregnated peat soils.

3.3 Dry Weight Experiment

To obtain the dry weight of peat, six different samples each weighing 15 g were placed in the oven for 24 hours at 110 °C (Mondal et al., 2007; Poots and McKay 1978)

3.4 Method for Peat Impregnation

The same concepts that Gu et al. (2005) used for impregnating AC were followed but the procedure was slightly different. The procedure for impregnating the horticultural peat is explained below:

1- 15 g of peat were added to four 150 ml $FeCl_2$ solutions of concentrations 1, 0.5, 0.1, 0.05 M. Fe^{2+} was used because it is easier to diffuse to inner pores than Fe^{3+}.

2- A 4 M NaOH solution was prepared for pH adjustment every 1½ hours for the first 6 hours, and every 6 hours for the rest of the 24 hours, which was the duration of the experiment.

3- The pH was adjusted to make sure that it fell in the range between 4.5 to 5, which is the perfect range for Fe^{2+}adsorption.

4- Sodium hypochlorite (NaClO) was added after six hours to oxidize iron (II) to iron (III) which forms stronger bonds with organic matter.

5- NaClO was added 2 times after that at an interval of six hours followed by pH adjustment.

6- Samples were continuously shaken during the 24 hours to insure proper mixing.

7- After 24 hours the solution and suspension were separated by centrifuging.

8- The quantity of iron impregnated was measured by subtracting the iron content of peat before impregnation from that after impregnation. The iron content was measured following the acid digestion method (3050 B).

9- The impregnated soil was washed and stored for the characterization and adsorption experiments (Gu et al., 2005).

3.5 Batch and Column Studies

For studying the adsorption capacity of soils, two experimental techniques were used, and they are batch and leaching column tests. The first test measures the adsorption capacity for a soil suspension in a solution having a certain concentration of contaminant while the

second measures the retention of a contaminant when passing a contaminated solution through a packed structure of soil (Yong et al., 1992).

In the Batch equilibrium test, solutions with different contaminant concentrations are used to examine the maximum amount that the soil suspension can adsorb. A soil to solution ratio of 1:10 is recommended by EPA and the mixture should be left till it reaches equilibrium which should not take more than 24 hours in common practice. For separation of the solid and liquid phases, a filter or a centrifuge is used. The amount of adsorption is measured using the following equation: $q = [(C_o - C) V] / M$

where q is the quantity of adsorption (g of contaminant/ g of soil), C_o and C are the initial and final concentration of contaminant in the solution respectively [g/ml], V is the volume of the solution [ml] and M is the mass of adsorbate [g]. Isotherms can be used to detect the relations between the concentration and quantity of adsorption (Yong et al., 1992).

In this study, 160 ml Arsenic solutions were prepared and mixed with 16 g of untreated peat as well with the impregnated soils. Dried impregnated soils were crushed into small particles using a mortar and pestle before mixing. The soil suspensions and solutions were placed on shaker for 24 hours then separated using a centrifuge. 100 ml of each solution was diluted to 250 ml in order for it to be tested with Arsenic kit while the remaining samples were analyzed using ICP-MS. The model of ICP-MS used for detecting Arsenic, after the batch and column tests, and the Fe concentration before and after impregnation, was HP4500 ICP-MS and the manufacturer was Hewlett-Packard.

250 ml is the volume of sample required for Arsenic detection by the kit to obtain accurate results. The minimum concentration that can be detected by the kit is 4 μg/l. According to the above dilution, a concentration of less than 4μg/l indicates that the concentration in the original sample is less than 10 μg/l. The Arsenic concentration in the solution was measured before and after the batch test to calculate the quantity adsorbed. Solutions were filtered through a 0.45 μm filter and then acidified with HNO_3 before detecting the Arsenic level.

The leaching column test is made to simulate the behavior of soil to contaminated water passing through soil. Only part of the soil will share in the adsorption process while the rest will not be exposed to contaminants. This test soil was packed in a column, for lateral confinement, with porous ceramic plates at both ends to allow the solution but not the soil to pass through. Break through curves were obtained by plotting the concentration of effluent/ original concentration of influent against time or pore volumes (Yong et al., 1992). The original solution and effluent were filtered through a 0.45 μm filter and then acidified with HNO_3 before detecting the Arsenic level using ICP-MS.

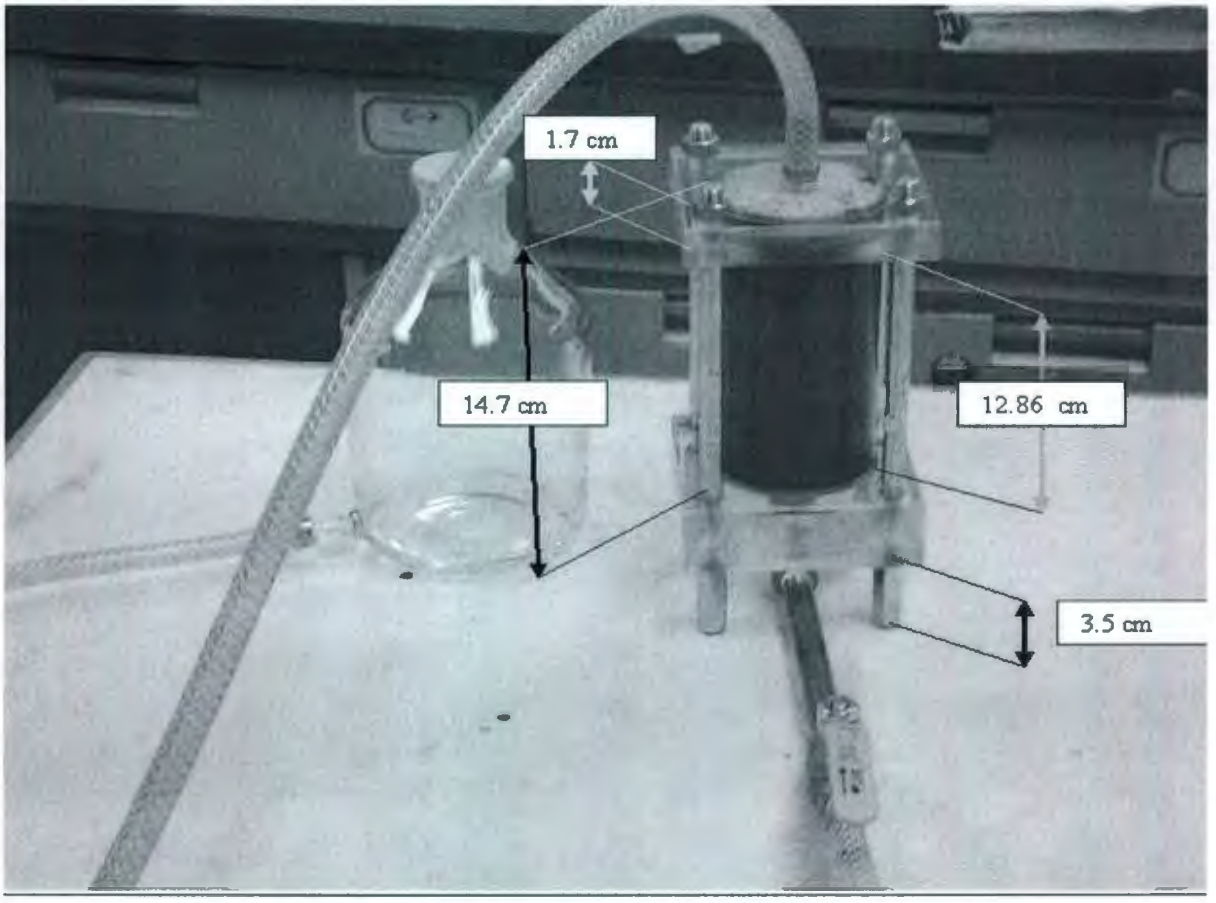

Figure 3.1. Column used for column test

The above photo shows an aspirator on the left and a column packed with soil on the right connected with a hose. The Arsenic solution was poured into the aspirator that was placed at a higher level than the column (1.55 m from the inlet of the column) for more head pressure. The water flowed through the column to be treated and was collected from the hose connected to the valve at the other end. The valve can be used to control the flow out and control the water residence time inside the column.

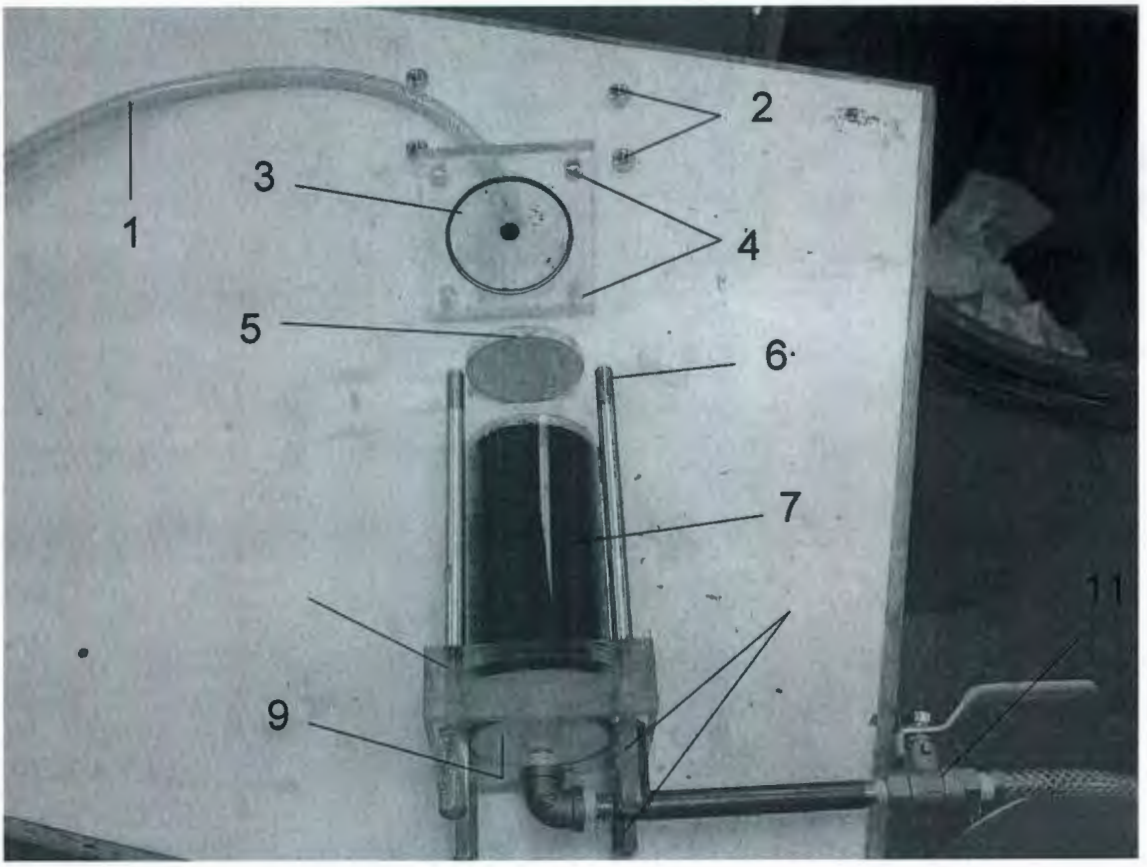

Figure 3.2 Components of the column used

The Figure above shows the various components of the column used which are

1- Hose: it connects the aspirator to the column.

2- Nuts: screwed around the threading of the bolts to tighten or loosen the components of the column together.

3- Upper plate: it has a grove so that the upper part of the confinement cylinder will fit snuggly inside. Round its edge a gasket is fixed to avoid seepage of water and to make sure that solutions are going through the column. It is made of acrylic which was purchased from E M Plastics.

4- Holes: Made so that the threading of the bolts will pass through the upper plate in order for the nuts to be tightened to hold the top plate in place.

5- Upper ceramic plate: it fits in a grove at the top of the confinement cylinder. It has an approximate porosity of 50 % by volume, pore size of 6 μm, and hydraulic conductivity of 5.11×10^{-5}. The aim of using a top plate is to make sure that the solution will be distributed along the whole cross section area of the column. Moreover, the plate will control the flow of solution into the column. The plates were purchased from Hoskins Scientific.

6- Aluminum Spacers: holding the upper plate with the nuts at the top and the lower plate and the cylinder in between by the legs at the bottom.

7- The confinement cylinder: it is made of acrylic which was obtained from E M Plastics. Its purpose is to contain the compacted soil. It has a diameter of 6.97 cm and height of 12.86 cm.

8- Lower plate: it has a grove so that the lower part of the confinement cylinder will fit in. It is a mirror of the upper plate and is made from the same material.

9- It is similar to the upper ceramic plate, yet it has a different purpose. It allows solution but not soil to flow out of the column.

10- Brass Legs: They help the column to stand without any extra support. They are made longer than the bend installed at the bottom of the column for taking the treated solution out.

11- Valve and tubing: the tubing is made of polycarbon manufactured by

Mc Master-Carr. The valve can be used to control the flow and the residence time of the solution in the column.

3.6 Arsenic Detection with ICP-MS and Test Kit

The kit used for determining the Arsenic concentration was the La Motte kit. It consists of two containers, two types of cover caps, a color chart, three different reagents, scoops for adding the reagents and a mercuric bromide pad. The three different agents are added consecutively with different concentrations, using specified scoops, to the Arsenic solution. The solution is shaken for a certain period after adding each solution to insure proper mixing. After shaking, the cap should be changed with the other one, which has a flip top with a spout to fit the mercuric bromide pad in. After the test, the pad is slowly removed from the spout to be compared to the color chart to obtain the Arsenic concentration. The Arsenic test kit is designed to measure Arsenic level between 4 and 100 µg/l (Spears et al., 2006). However, it was found that the La Motte test kit was not accurate for determining low As concentrations between 29.84 and 62.61 µg/l (see the comparison between the La Motte test kit and the ICP-MS, second and last columns in Table 4.7)

The reaction involved can be simplified as follows. Zinc dust is added to the Arsenic sample in an acidic medium which changes Arsenic from its aqueous form to arsine gas. The gas emitted reacts with the mercuric bromide pad forming a yellow to brown color compound, AsH_2HgBr. The darker the color formed the more the concentration of Arsenic in the sample tested. The pad color is compared to a color chart indicator to determine the corresponding Arsenic concentration to the color obtained (Spears et al.,

2006). Samples were analyzed by both the La Motte kit and ICP-MS to check the accuracy of the kit.

3.7 Minitab

Minitab was used in this study to statistically analyze the data obtained from the government of Newfoundland and Labrador for the contaminated abandoned sources as well as the results from analyzing treated water samples using ICP-MS. Two different analyses were done using Minitab and they included a correlation and a principal component analysis. For both analyses, 31 different parameters in addition to Arsenic were included. Parameters can be classified into chemical parameters and physical properties. Chemical parameters included in the analysis were the concentrations of boron, bromide (Br-), calcium, chloride, fluoride, potassium, sodium, sulfate, ammonia, nitrate, nitrite, phosphorus, aluminum, antimony, barium, cadmium, chromium, copper, iron, lead, magnesium, manganese, mercury, nickel, selenium, uranium, and zinc present in water while physical properties are pH, total dissolved solids, turbidity, alkalinity, conductivity, and hardness. The values and concentration of parameters for the 128 samples, taken from different sources and areas in Newfoundland, were used for the correlation.

The province was divided into three regions eastern, central, and western. The significance of the correlation obtained from Minitab was decided according to the values in Table 2.5 under the 0.05 p-value column, which is the p-value that Minitab uses as a set default. The values in Table 2.5 are the minimum accepted values for a significant correlation at a given number of samples. The df used for each region was the number of samples taken from the region's sources, minus two. Accordingly, the df for eastern, western and central regions were 85, 23, and 14 respectively. The eastern part especially the Avalon Peninsula was the most populated region. It was also the one with higher numbers of contaminated sources and higher values of Arsenic in water when compared to the central and western regions. However, in Labrador, Arsenic concentration in drinking water has not been found to be a problem (Guzzwell, personal communication, 2005).

Chapter Four

Results

The results of the characterization, column and batch tests are presented in this chapter. Calculations and Tables for the PZC (Tables A.6 to A.10) are presented in Appendix A.1 and A.3.2 respectively. Correlations between Arsenic and all the other physical properties and chemical parameters of Newfoundland water sources in the eastern, western and central regions of the province are shown in Appendix A.3.1, Tables A.2 to A.5.

4.1 Characterization Results

The experimental work started with three characterization tests which were PZC, CEC, and acid digestion for treated and untreated peat. The aim was to determine the charges

on peat at various pH levels, the ability of impregnated and untreated peat to exchange cations, and both arsenic and Fe contents of peat before and after impregnation

4.1.1 Point of Zero Charge

Five experiments were done for determining the PZC for untreated peat and the 4 treated peats. The experiments were carried out to detect the effect of impregnation and the initial concentration of Fe in the impregnating solution on the PZC of peat. Moreover, the PZC is a very important factor that helps in understanding the behavior of different metals and elements during their adsorption on substrate surfaces. Since untreated soil and one of the impregnated soils were to be used for column studies, the PZC of all the impregnated soils and untreated peat was measured.

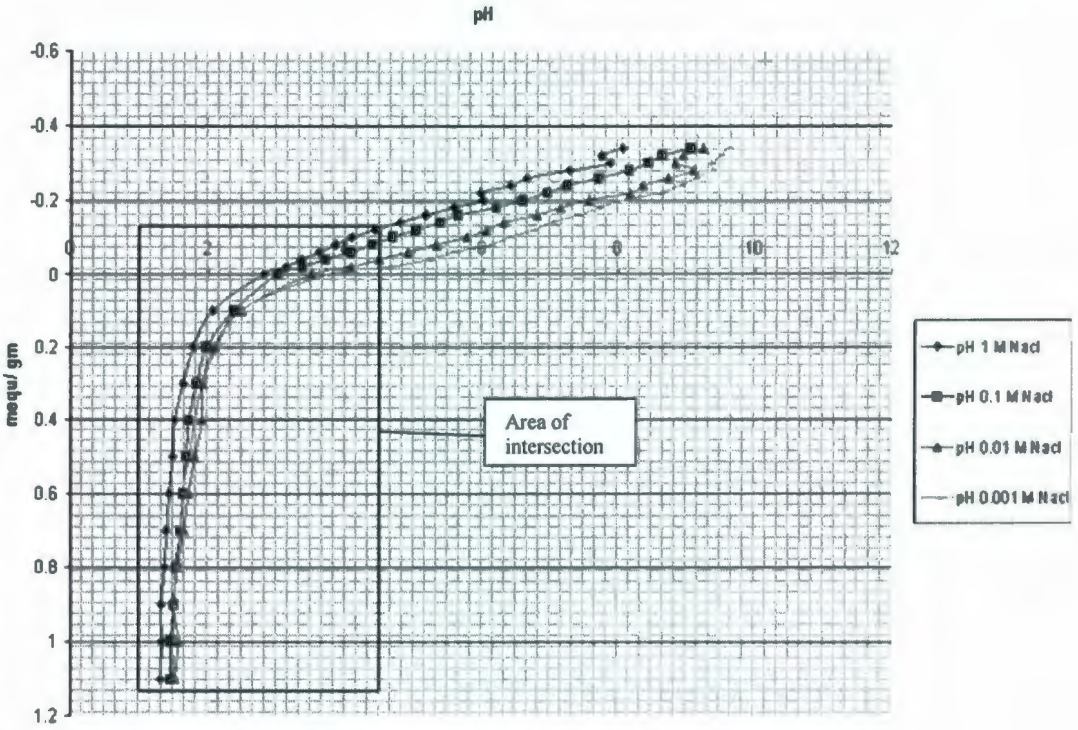

Figure 4.1 Titration curve for determining the PZC for the untreated peat

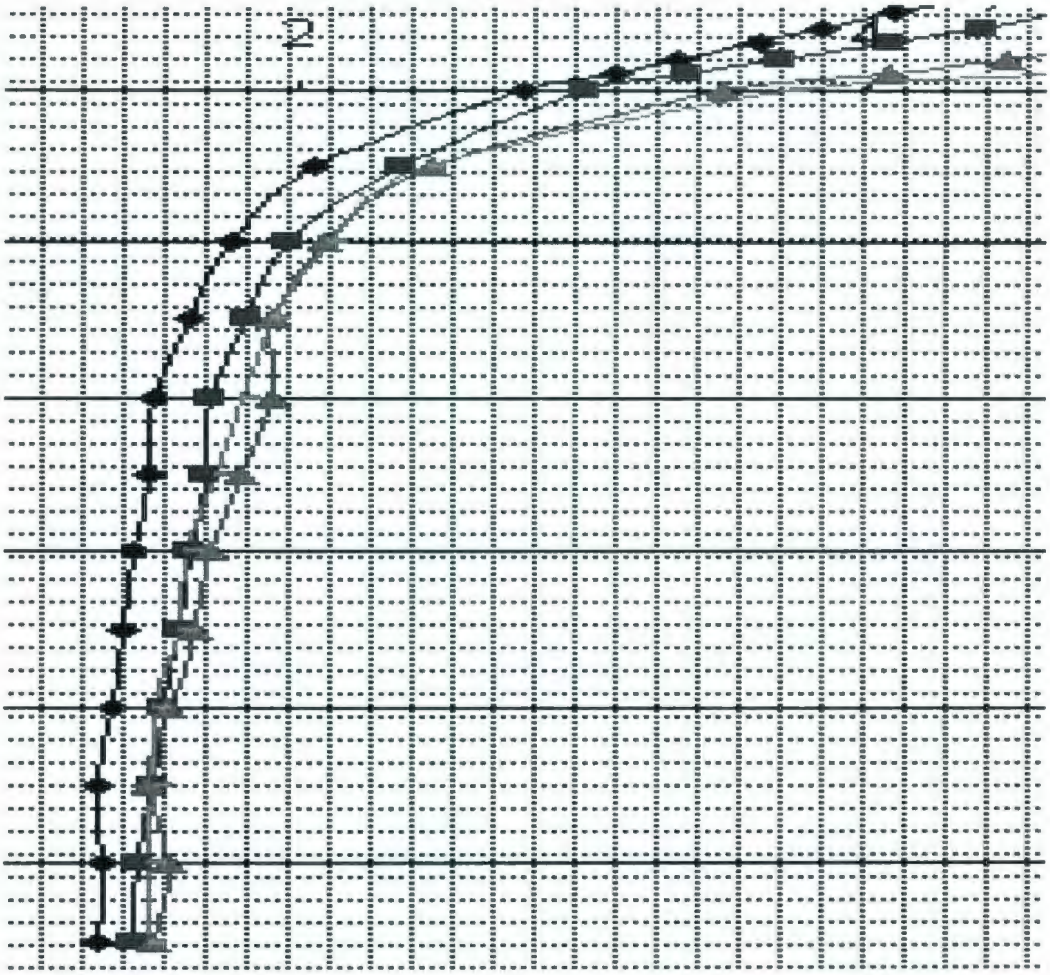

Figure 4.2. Zooming on the area of intersections of untreated peat curve (the area marked above in Figure 4.1)

Figure 4.1 shows that the black line (with diamond markers) representing the data obtained from titration of 1M NaCl solution did not intersect those of the 0.1M NaCl (with rectangular markers), 0.01M NaCl (with triangular markers), and 0.001M NaCl (with dash markers). Figure 4.2 zooms in on the area of intersections which shows that the rest of the lines intersected between pH 1.5 and 2.5. The lines intersected at pHs 1.5, 1.6, 1.7, 1.9, 2.1 and 2.5. Therefore, the PZC was between these values and the pH_{PZC} was approximately equal to 2.

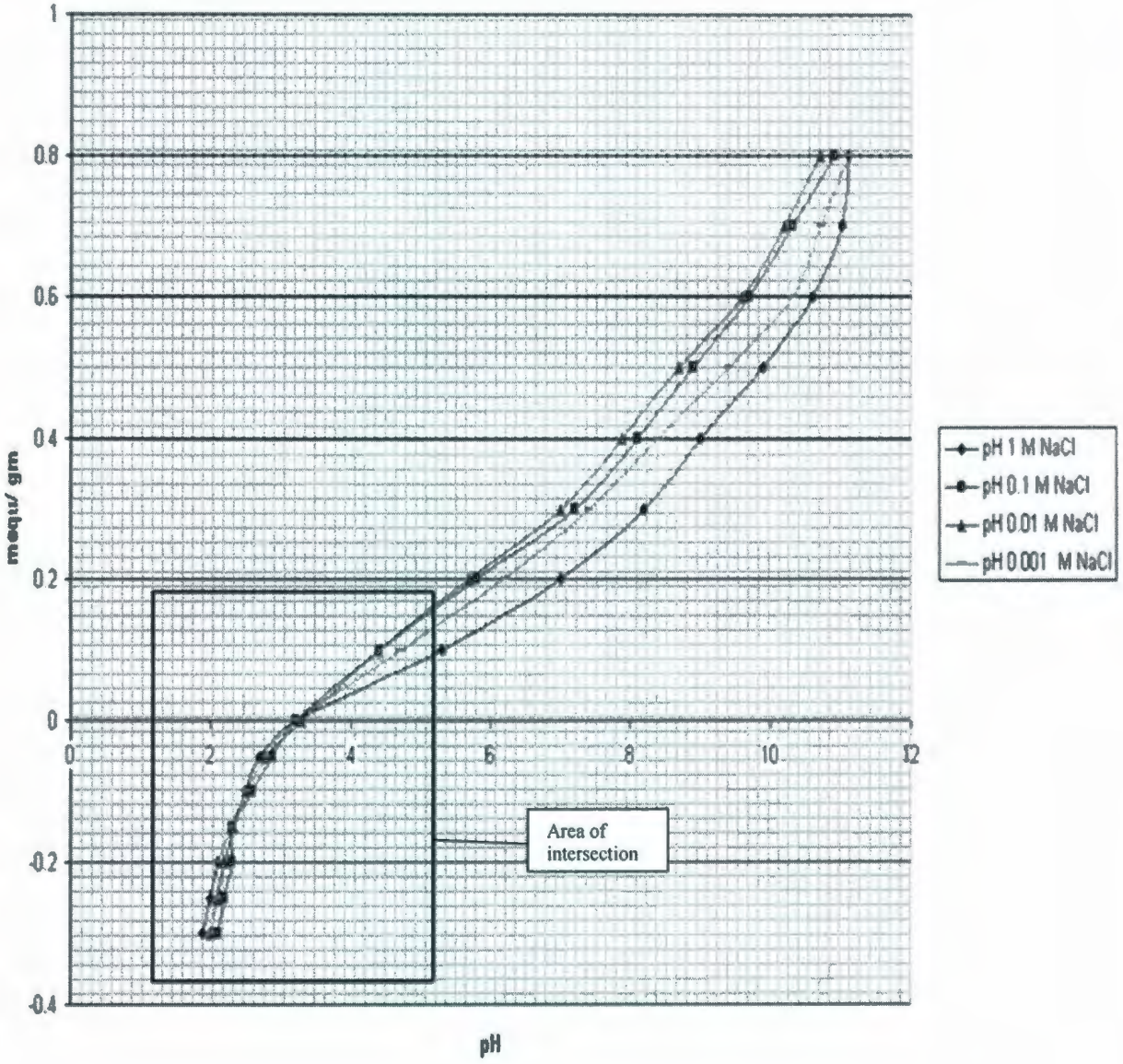

Figure 4.3. Titration curve for determining the PZC of the peat impregnated with 1.08 M Fe (Fe 1.08-Peat)

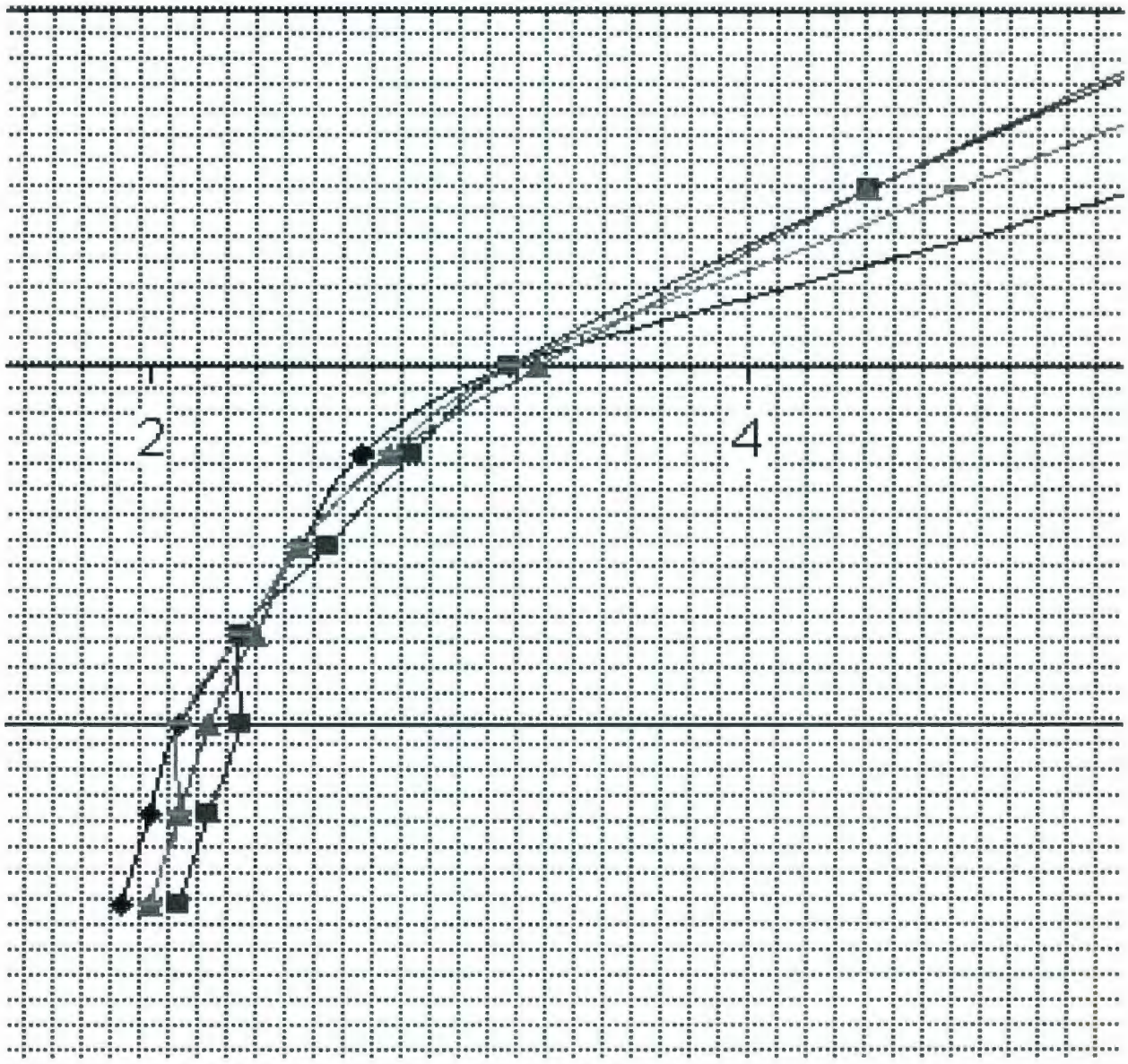

Figure 4.4. Zooming on the area of intersections of 1.08 Fe-Peat (the area marked above in Figure 4.3)

Figure 4.3 shows that the black line (with diamond shape markers) representing the behavior of the suspension in 1.08M NaCl solution had the highest pH after the base was added, though it should have had the lowest pH. Moreover the red line (with triangular markers) representing the suspension in 0.01 m NaCl should have had a lower pH than

that of the blue (with the rectangular markers). However their pH values were very close to each other. Ignoring the black line (with the diamond shape markers), Figure 4.4 shows that the rest of the lines started intersecting at pH 2.3 and kept intersecting till reaching a pH value of 4.4. Accordingly the pH_{PZC} was between these two values and was approximately equal to 3.3.

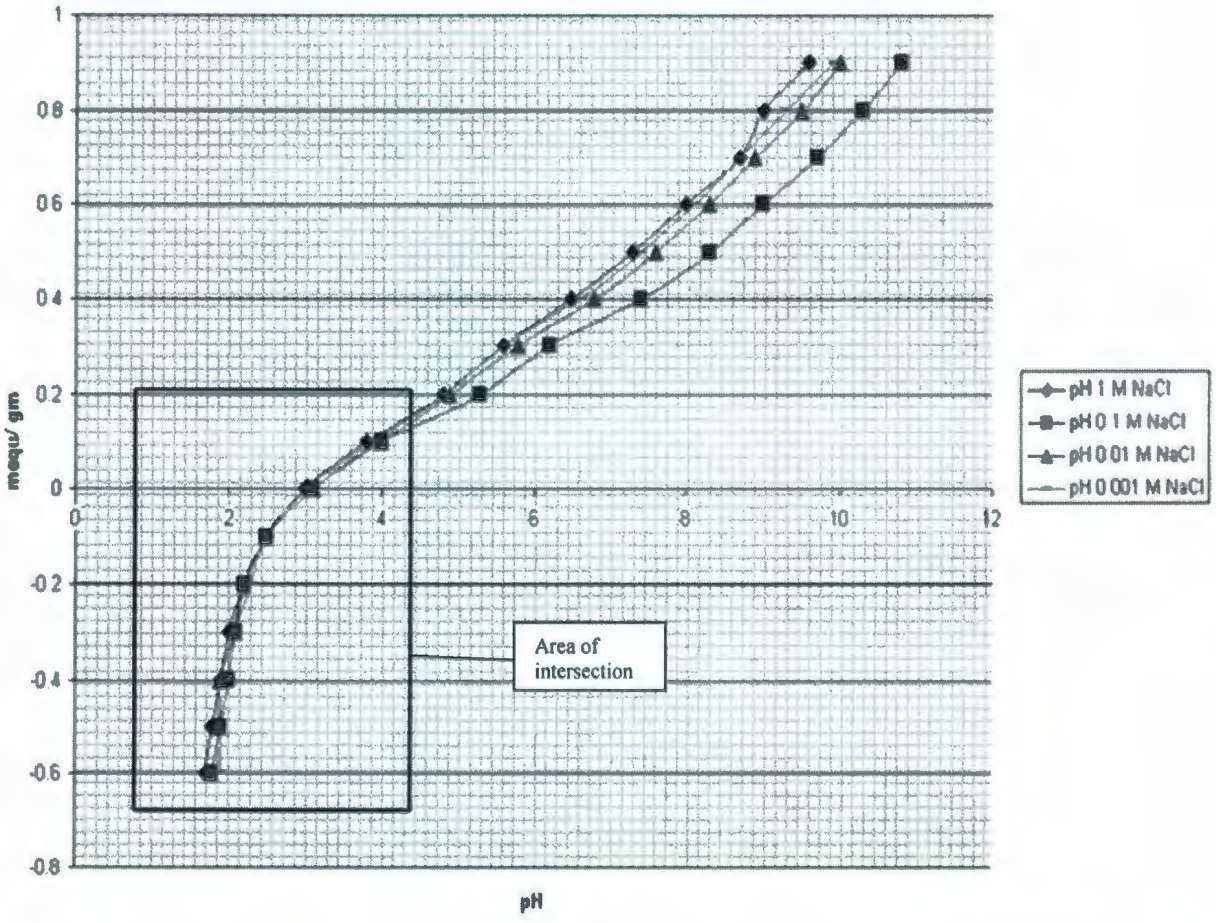

Figure 4.5. Titration curve for determining PZC of peat impregnated with 0.54 M Fe (Fe 0.54-Peat)

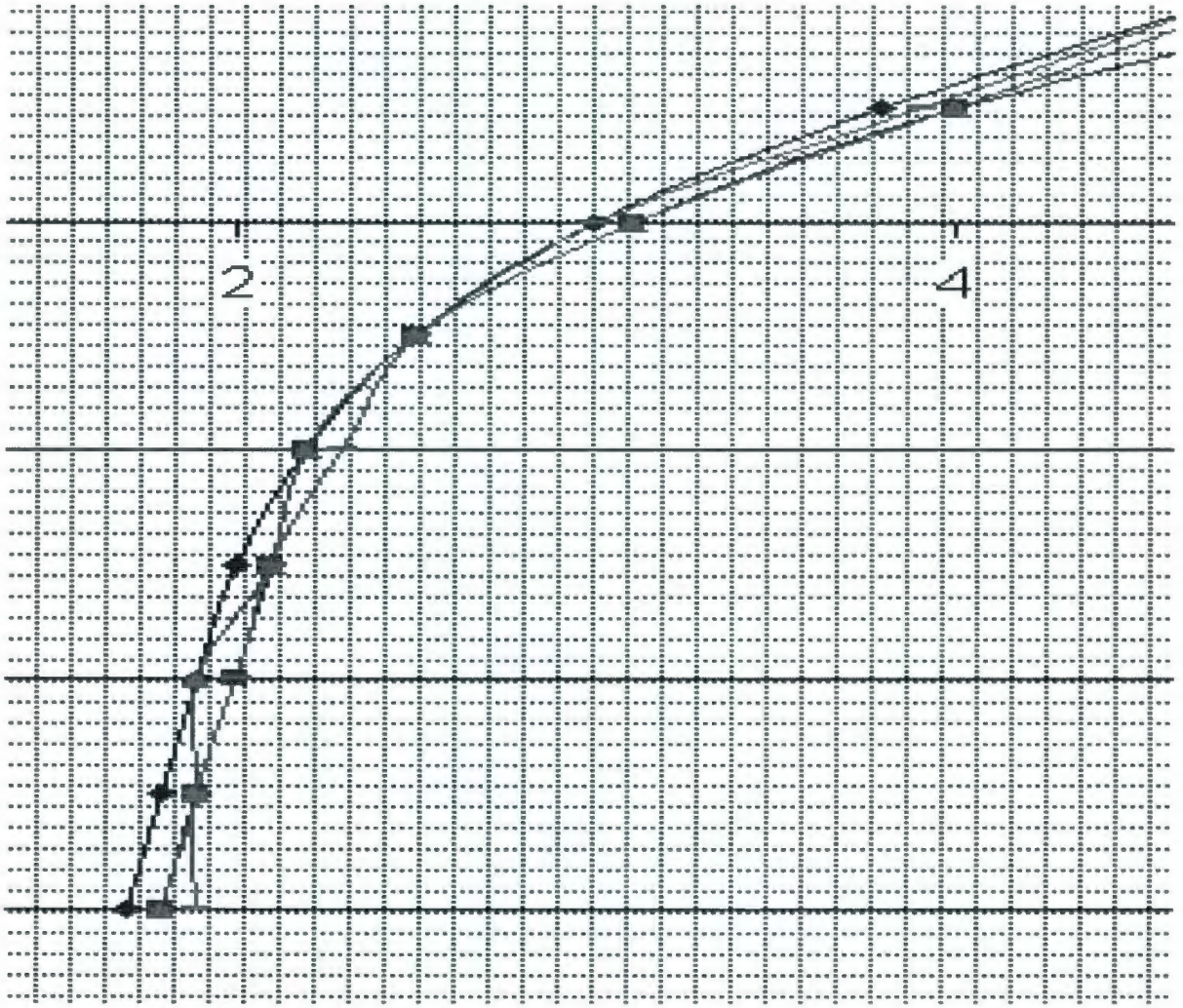

Figure 4.6 Zooming on the area of intersections of Fe 0.54-Peat(the area marked above in Figure 4.5)

Figure 4.5 shows that the lines representing the behavior of suspension in NaCl solutions should have pH values decreasing in the following order green (with the dash markers representing 0.001 M NaCl) > red (with the triangular markers representing 0.01 M NaCl) > blue (with the rectangular markers representing 0.1 M NaCl) > black (with the diamond markers representing 1 M NaCl). However, the green line (with the dash markers) representing the soil suspension in 0.001 M NaCl was having the lowest pH and

it kept intersecting with the black line (with the diamond markers). Therefore, the green line was neglected. Zooming in on the area of intersection, Figure 4.6 shows that the blue line (with the rectangular markers) and the red line (with the triangular markers) kept intersecting till the red got on top of the blue, though their pH values were close. The lines kept intersecting starting at pH 1.9 and ending at pH 4.1. Accordingly, the pH_{PZC} was between theses two values and was approximately equal to 3.

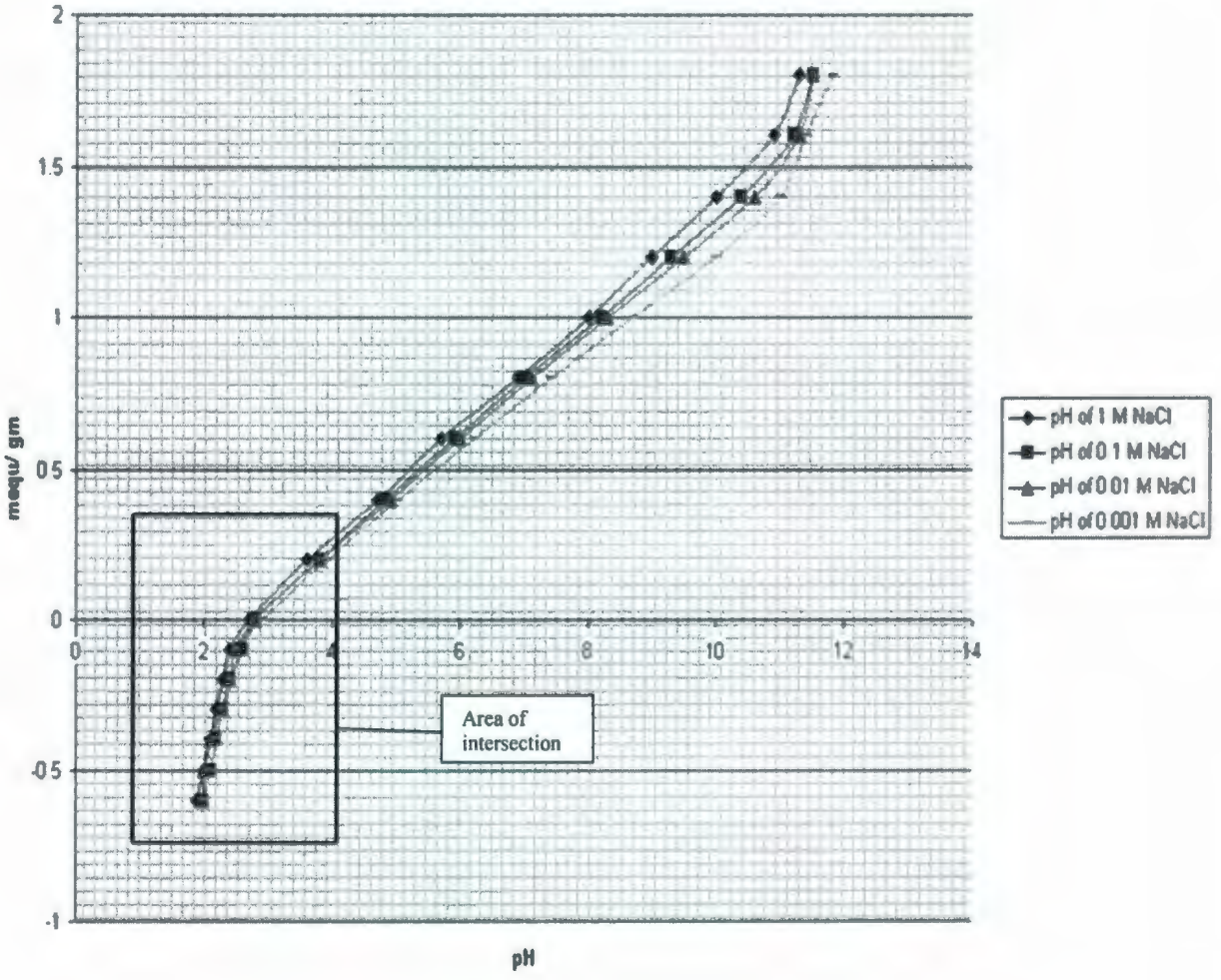

Figure 4.7 Titration curve for determining PZC of peat impregnated with 0.108 M Fe (Fe 0.108-Peat)

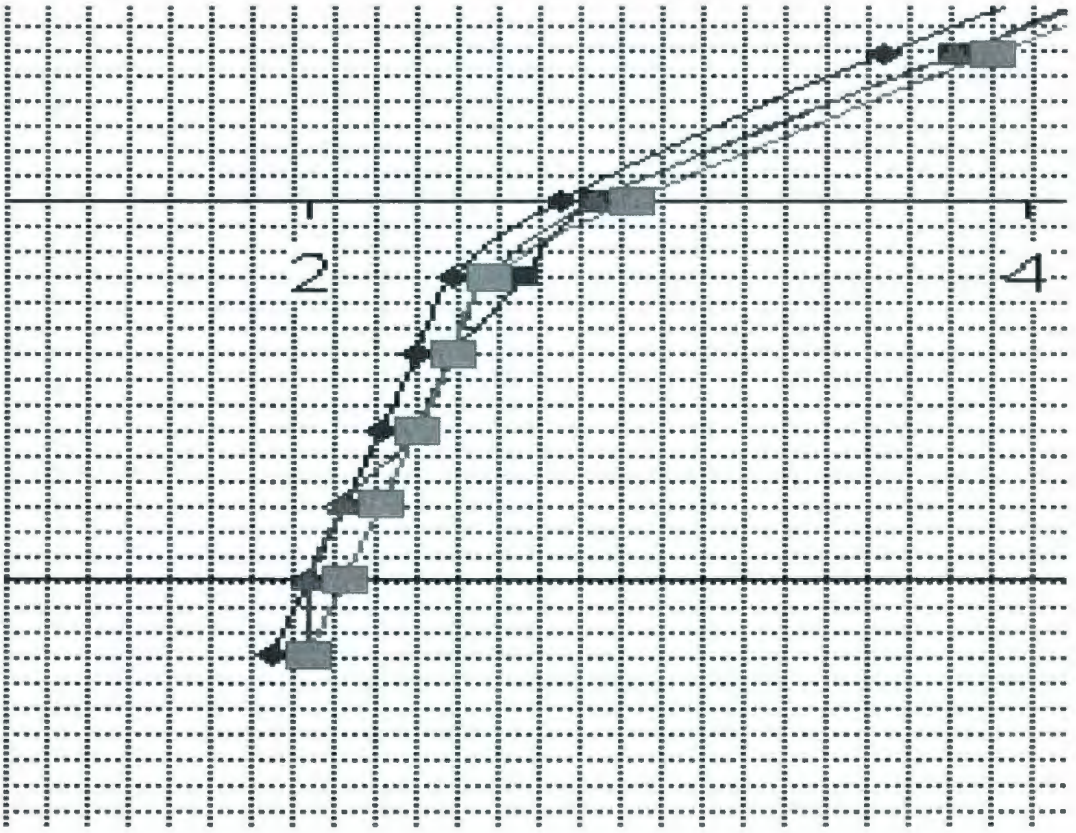

Figure 4.8 Zooming on the area of intersections of Fe 0.108-Peat (the area marked above in Figure 4.7)

Figure 4.7 shows that the positions of all lines were perfect and that the lines representing the behavior of the NaCl solutions, after adding the base, had pH values decreasing in the following order Green (with the dash markers representing 0.001 M NaCl) > Red (with the triangular markers representing 0.01 M NaCl) > Blue (with the rectangular markers representing 0.1 M NaCl) > Black (with the diamond markers representing 1 M NaCl). In Figure 4.8, the intersection of the lines started at pH 2 and ended at pH 3.8 and so the pH_{PZC} was around 2.9.

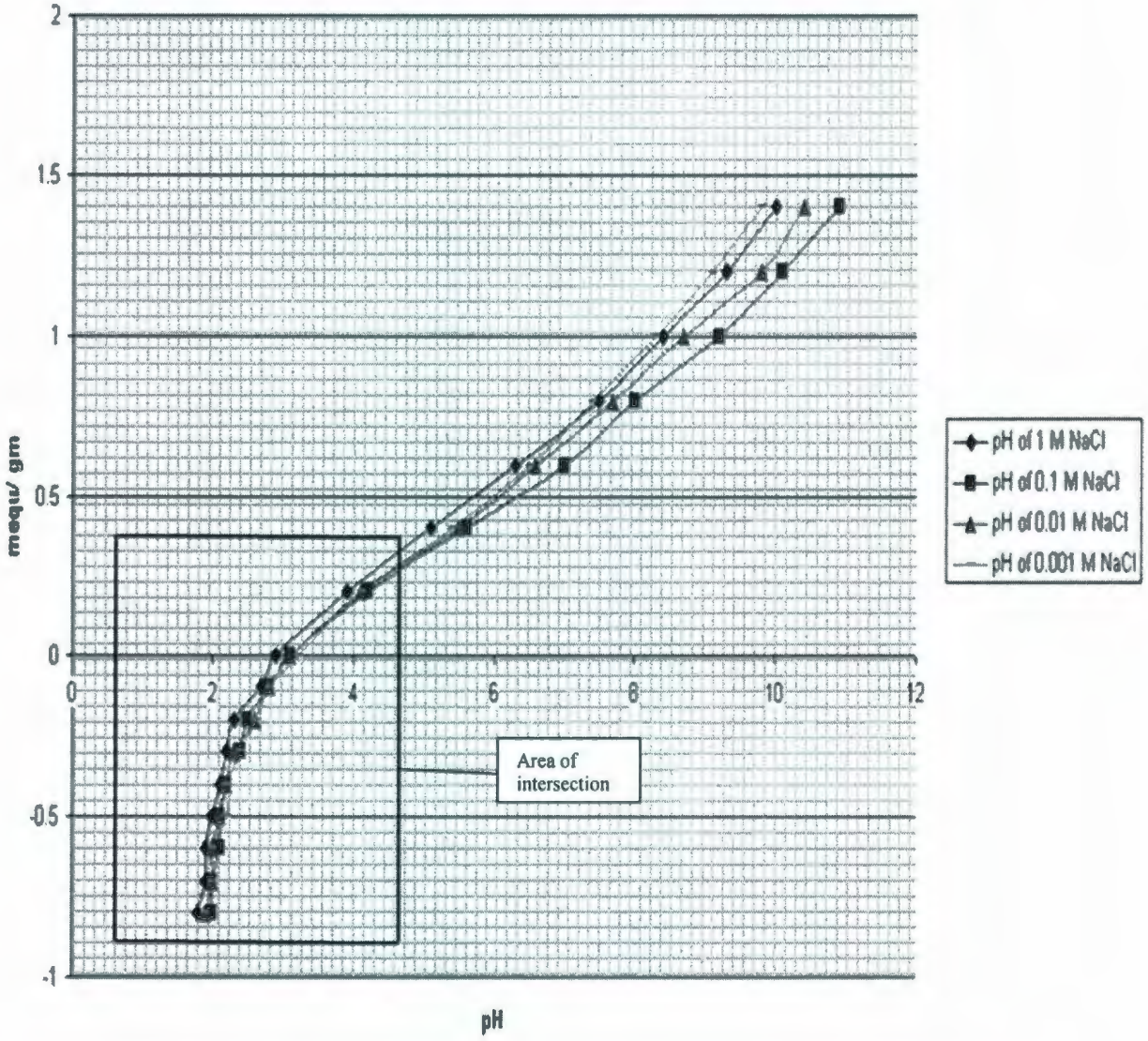

Figure 4.9 Titration curve for determining PZC of peat impregnated with 0.054 M Fe (Fe 0.054-Peat)

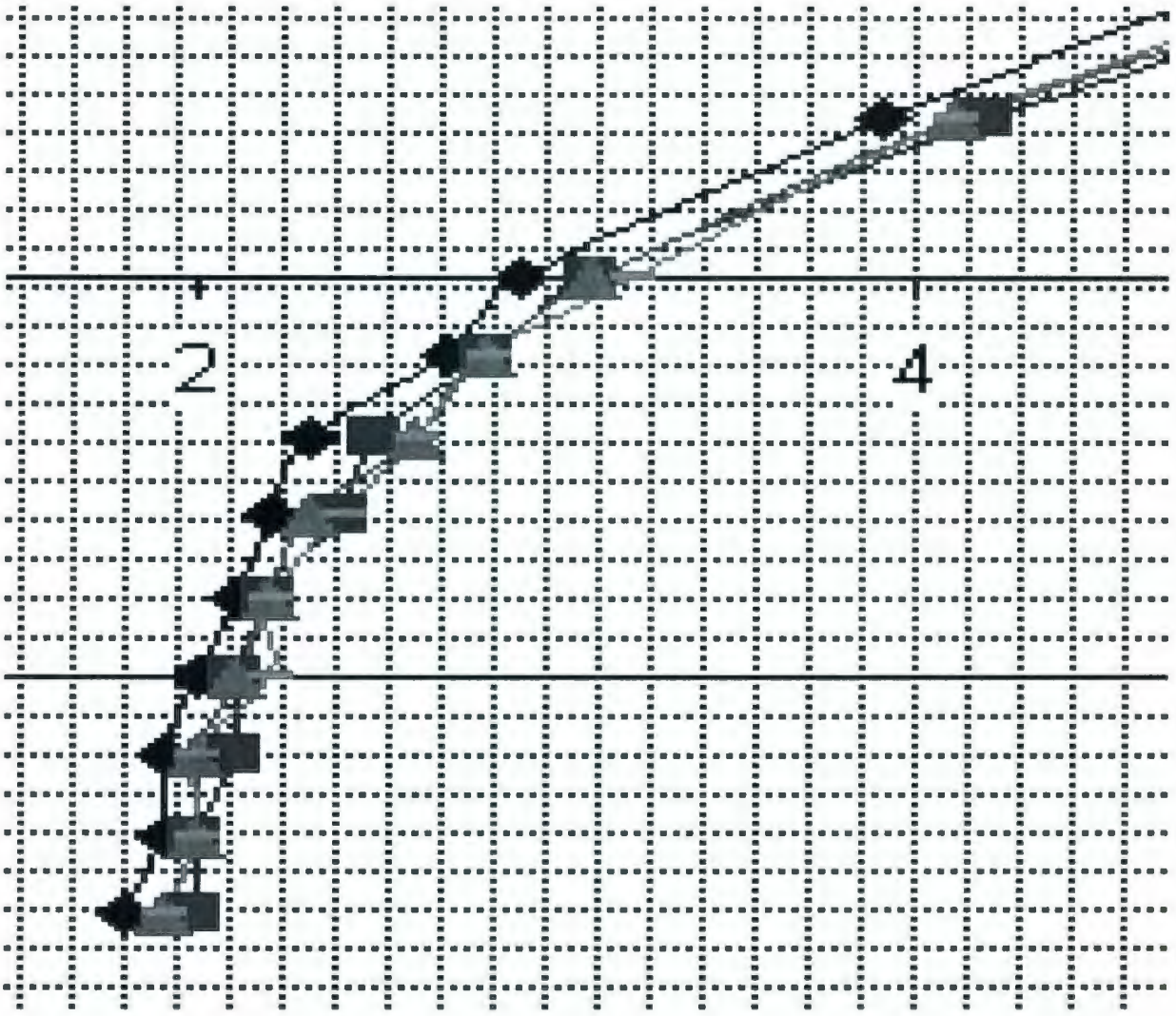

Figure 4.10 Zooming on the area of intersections of Fe 0.054-Peat (the area marked above in Figure 4.9)

Figure 4.9 shows that the green line (with the dash markers) representing the soil suspension in 0.001 M NaCl was having the lowest pH and it kept intersecting with the black line (with the diamond markers representing 1 M NaCl), although the green line should have had the highest pH values. Therefore, the green line was neglected. In Figure 4.10 it is obvious that the blue line (with the rectangular markers representing 0.1

M NaCl) and the red line (with the triangular markers representing 0.01 M NaCl) kept intersecting till the red got on top of the blue, though their pH values were close. The lines kept intersecting starting from pH 1.9 and ending at pH 4.1. Accordingly, the pH_{PZC} was between these two values and was approximately equal to 3.

The results shown in Figures 4.1 to 4.10 are summarized in Table 4.1 and it can be seen that the highest level of Fe impregnation resulted in the greatest increase in the pH_{pzc} which was expected since an increase in the PZC of 0.7 to 1.2 has been observed before when impregnating activated carbon with Fe (Reed et al., 2000). After impregnation, the PZC increased by 1, 0.9, 1, and 1.3 pH units for Fe 0.054-Peat, Fe 0.108-Peat, Fe 0.54-Peat, and Fe 1.08-Peat respectively.

Table 4.1 PZC of untreated and impregnated peat

Peat	PZC
Untreated peat	2
Fe 0.054-Peat	3
Fe 0.108-Peat	2.9
Fe 0.54-Peat	3
Fe 1.08-Peat	3.3

4.1.2 Cation Exchange Capacity

The CEC tests were conducted to determine the effect of the impregnation on the free adsorption sites on the peat surface and whether or not this effect would have any influence on the Arsenic uptake during As adsorption.

Table 4.2 Cation exchange capacity for natural peat and the four impregnated peats

	CEC (mequ/100 g)			
Soil	First set	Second set	Third set	Average
Untreated peat	46.75	58.3	59.4	54.8
Fe 0.054-Peat	18.7	24.2	24.7	22.5
Fe 0.108-Peat	13.2	13.2	25.8	17.4
Fe 0.54-Peat	15.4	15.4	20.3	17.1
Fe 1.08-Peat	7.7	7.7	10.4	8.62

The results of the CEC experiments are presented in Table 4.2 and these tests were conducted in triplicate. By looking to the first and last columns in Table 4.2, it is obvious that the Fe concentration in solution during the impregnation process affected the CEC of the produced impregnated soil. There is a negative correlation between the CEC and the concentration of Fe in the impregnating solution. Peat has high organic content which is rich in functional groups. The exchange of the hydrogen ions attached to these groups

with Fe during the impregnation due to the formation of inner sphere complex or physical adsorption is the reason for the reduction in the CEC results obtained. The strong covalent bond that was formed between some of the functional groups and Fe and the preferential adsorption of Fe over Ca onto peat surface prevented any further exchange of Fe^{3+} by Ca^{2+} which was the ion used to detect the CEC of peat in this research (Brown et al., 1999).

4.1.3 Acid Digestion

The acid digestion tests were conducted to determine the Fe and Arsenic content of the peat soil samples, which included the untreated soil and the Fe impregnated peat soil samples (Fe-Peat). The test was done once for the untreated peat and each of the Fe-Peat soils which was enough to check if there was any trend due to the variation in Fe concentration in the impregnating solutions.

Table 4.3 Acid digestion results for five peat soil samples

	Metal content of peat soil samples			
The five peat soil samples	**Fe 54 (g/kg)**	**Fe 57 (g/kg)**	**Average Fe (g/kg)**	**As (mg/kg)**
Untreated peat	1.06	0.96	1.01	0.21
Fe 0.054-Peat	51.9	56.2	**54.1**	0.5
Fe 0.108-Peat	47.3	51.4	**49.4**	0.6
Fe 0.54-Peat	131	141	**136**	0.5
Fe 1.08-Peat	111	116	**114**	0.33

The results of the acid digestion in Table 4.3 show that the concentrations of Fe in the soil treated with 0.054 and 0.108M Fe solution were almost the same. The quantity of Fe impregnated increased by more than double that of the Fe 0.054-Peat and Fe 0.108-Peat when the initial Fe concentration in the Fe solution increased to 0.54M. However, the Fe content in the soil decreased when the impregnating solution concentration was increased to 1.08M Fe. This decrease was slight though, from 136 mg/kg to 114 mg/kg. The non linearity between iron content of peat and the Fe concentration in the impregnating solution might have occurred because peat was not homogenous especially that the peat used was not sieved. Peat was brought from a peat bog and was used as is and only large twigs and gravel were removed. Saturation is not an option in this case since lower concentration of Fe in the impregnating solution has led to higher Fe content of peat (as

in the Case of the Fe 0.54-Peat and Fe 0.054-Peat when compared to Fe 1.08-Peat and Fe 0.108-Peat respectively) (see Table 4.3, Average Fe column, the bolded values).

Increasing the concentration of Fe from 0.108M to 0.54M in the impregnating solution increased the amount of Fe retained on peat to more than double. However, the percentage of Fe adsorption decreased. The percentage of adsorption in the case of the Fe 0.108-Peat was 82 % which was calculated by dividing the retained 49.4 g Fe/kg soil (see the third last row of Table 4.3) by the 60 g Fe available in the impregnating solution for each kg of soil. For the Fe 0.54-Peat, the percentage of adsorption was 45% and it decreased further for the Fe 1.08-Peat with the decrease in the quantity of Fe adsorbed (see the last row in Table 4.3) versus the increase in the amount of Fe available in the solution and it was 19 %. The decrease in the percentage of adsorption with the increase of metal concentration in the influent has been documented before for Cu, Zn, and Ni (Viraraghavan and Dronamraju, 1993). The Arsenic content of peat increased as well with impregnation. This is because of the presence of 10 μg/g Arsenic as an impurity in the $FeCl_2$ which was also adsorbed with Fe onto the peat surface.

4.2 Dry Weight Test

The dry weight test was conducted to determine the water content of the horticultural peat.

Table 4.4 Dry weight of peat

Sample #	Weight of peat (g)	Weight of peat and container before drying (g)	Weight of peat and container after drying (g)	Net weight of peat after drying (g)
1	15	48.55	45.58	2.97
2	15	48.79	45.72	3.07
3	15	48.61	45.52	3.09
4	15	48.31	45.45	2.86
5	15	48.73	45.59	3.14
6	15	48.77	45.8	2.97
Average	15	48.63	45.61	3.01

For the dry weight test, six samples each weighing 15 g were tested. The average weight of peat after drying was 3.01 g. Accordingly, the moisture content of peat was about 80% or very high.

4.3 Batch Test Results

The batch tests were conducted to compare the adsorption capacity of the four Fe-Peat soils with each other and with the untreated peat as well. This was done by comparing the Arsenic concentrations in the solutions before and after they were treated with the five peat soils. Untreated peat and the Fe-Peat with the highest adsorption capacity were chosen for subsequently conducting the column tests.

4.3.1 The La Motte Arsenic Test Kit Results

The Arsenic solution treated with impregnated soils and untreated peat were tested using the Arsenic test kit. For the Arsenic sample treated with Fe 1.08-Peat, part of it was spilled and only 50 ml was left. 25ml was stored for Arsenic detection by ICP-MS and the other 25 ml was not enough to obtain decent results with the Arsenic test kit. This is because after diluting the 25 ml to 250 ml, the volume required to obtain an Arsenic reading, an Arsenic level below the 4 ppb detection limit of the kit was obtained. This meant that the sample before dilution had an Arsenic level below 40 ppb. This result included a very wide range of Arsenic levels which neither helped to determine whether

the sample had a concentration less than the allowable 10 μg/l limit for drinking water nor helped to detect the amount of Arsenic adsorbed onto the Fe 1.08-Peat surface. Additional samples should have been prepared as a backup in case of human errors during the tests. This would have allowed the use of samples without dilution and hence getting more accurate results and the extra samples would have been used in case of spillage (as in the case of the sample treated with Fe 1.08-Peat) to obtain results for all treated samples from the arsenic test kit.

For the Arsenic sample treated with unimpregnated peat, after adding the three reagents of the kit, bubbles started coming up until they reached the mercuric bromide pad which became wet and so no result could be obtained. The pads are designed to detect the arsine gas emitted after adding the reagents to arsenic solutions. Pads should always be kept and stored dry since moisture can destroy the pad and affect the results obtained. For the As samples treated with Fe 0.54-Peat and Fe 0.108-Peat, 92 ml of each sample were diluted to 250 ml and the result obtained for the Arsenic limit was less than 4 ppb for both, which reflects a concentration of value less than 10.86 ppb before dilution. For the Arsenic sample treated with Fe 0.54-Peat, 89 ml was diluted to 250 ml to be tested. The concentration detected was less than 4 ppb indicating a concentration of less than 11.8 ppb in the original sample before dilution. These results are all summarized in Table 4.5.

Table 4.5 Arsenic test kit results for the batch tests (solution to soil ratio of 10:1)

Sample tested	As test kit results
Effluent after treating with untreated peat	Bubbles were produced which came into contact with the mercuric bromide pad
Effluent after treating with Fe 1.08-Peat	Part of the sample was spilled. The amount left was not enough to obtain results
Effluent after treating with Fe 0.54-Peat	Less than 10.86 ppb
Effluent after treating with Fe 0.108-Peat	Less than 10.86 ppb
Effluent after treating with Fe 0.054-Peat	Less than 11.2 ppb

4.3.2 ICP-MS Results

The ICP-MS was used to measure the Arsenic concentration for the same solutions that had been previously tested using the La Motte test kit. The ICP-MS is an EPA approved and accurate method for detecting As levels (Spears et al., 2006). It was used in this study to evaluate the accuracy of the La Motte test kit and to insure that the results obtained were reliable and accurate especially since the Arsenic level for most of the tested solutions in this study ranged between 1 and 63 μg/l which were very low concentrations. The results of the ICP-MS are listed in Table 4.6 and represent three sets of batch test experiments. The first and third sets were conducted at a soil to solution ratio of 1:10 while the second was conducted at a ratio of 2:10. The third test was a blank test in which each of the five peat soils were added to distilled water rather than contaminated water.

The first row of the Table represents the properties (pH and As and Fe concentrations) of the three initial solutions used for the three batch tests while the rest of the rows represent the properties of the solutions after they were treated with the five peat soils. For the initial solutions of the first and the second batch tests, the average Arsenic concentration was 60 μg/l. For the third test or the blank test, the Arsenic level in the initial solution was 7.84 μg/l which is high concentration for distilled water. This distilled water was obtained from the Environmental Lab in the Engineering Building. The distilled water in the Earth Sciences Lab was later found to have an Arsenic concentration ranging between 0.7 to 2 μg/l. To obtain more accurate results for blank tests in the future, a pure distilled water supply is recommended.

Table 4.6 ICP-MS results for the batch tests

	Batch tests Soil water ratio of 1:10			Batch tests Soil water ratio of 2:10			Blank test Soil water ratio of 1:10		
Solutions	As conc. µg/l	pH	Fe released to solution mg/l	As conc. µg/l	pH	Fe released to solution mg/l	As conc. µg/l	pH	Fe released to solution mg/l
Initial conditions	62.61	5.4	0.589	57.4	5.5	0.185	7.84	5.5	0.19
Solution treated with regular peat	51.7	3.9	0.519	34.3	4.0	0.656	4.36	4.4	0.42
Solution treated with Fe 0.054-Peat	64.0	3	1,127	117	2.9	660	141	3.0	209
Solution treated with Fe 0.108-Peat	67.9	2.5	1,726	181	2.3	140	106	2.6	147
solution treated with Fe 0.54-Peat	**29.8**	3.1	275	**90.1**	3.1	211	**32.9**	3.2	68
solution treated with Fe 1.08-Peat	44.7	3.2	96	**88.4**	2.8	275	138	3.3	191

The ICP-MS results indicated that 0.54M-Peat was the most effective impregnated peat in removing Arsenic at a soil to solution ratio of 1:10 (see first column of Table 4.6). The Arsenic concentration was reduced to less than half the initial concentration. The increase

in Arsenic concentration when the solutions were treated with Fe 0.108-Peat and Fe 0.054-Peat was most probably due to the presence of Arsenic as an impurity in the $FeCl_2$ solvent. The label on the $FeCl_2$ used stated that the Arsenic concentration was 0.001 % or 10 μg/g. This means that impregnated peat released arsenic which increased the arsenic concentration in the initial solution. This also means that the quantity of arsenic removed by peat was even higher than the value that can be obtained from Table 4.6 (by subtracting the arsenic concentration of the treated solution from the arsenic concentration of the initial solution). However, batch tests were carried out just to compare the adsorption capacities of impregnated peat soils to choose the best adsorbent for further experimentation using column tests and not to measure these capacities.

The adsorption capacity of the Fe 0.108-Peat and Fe 0.054-Peat soils was not enough to retain the Arsenic adsorbed during Fe impregnation (see Table 4.3) and to adsorb the As in the spiked solution as well. In contrast, Fe 0.54-Peat and Fe 1.08-Peat were having a higher adsorption potential and were able to adsorb Arsenic from the solution in addition to the retained As during the impregnation. This happened despite the Arsenic content in Fe 0.54-Peat and Fe 1.08-Peat that was built up during the impregnation process.

There is another correlation that can be observed from Table 4.6. With few exceptions, the amount of iron released to the solution was negatively correlated to the pH. The higher the pH value the lower the quantity of Fe released from the treated peat. This could happen because the higher pH is resulting in increasing the negative charges of the soil which increased the ability of the soil to retain the adsorbed Fe.

For the 1: 10 batch test, the Arsenic uptake was positively correlated to the Fe concentration in the impregnating solution except for the Fe 1.08-Peat. This possibly happened due to the blocking of inner pores of peat by iron oxyhydroxide, which increased due to the increase of iron levels in the impregnating solution (Gu et al., 2005). Blocking the pores reduced the uptake of Arsenic and that might be the reason for the reduction in Arsenic uptake.

The second set of batch experiments conducted with a soil to solution ratio of 2:10 was carried out to test whether the assumption of blocking the pores of peat when using more Fe during impregnation was correct or not.

For the soil to solution ratio of 2:10, regular peat showed the best adsorption results while solutions treated with impregnated peat had a higher Arsenic concentration than that in the initial solution. The increase in Arsenic levels was believed to be due to the Arsenic impurities in the $FeCl_2$. This is why the Arsenic levels increased with the increase in the soil to solution ratio. On the other hand when comparing the Arsenic levels of the solutions treated with Fe-Peat soils together, it is obvious that Fe 0.54-Peat and Fe 1.08-peat were the best substrates (see the bolded values in the fifth column of Table 4.6). They had almost the same adsorption capacity, accordingly, the Fe 0.54-Peat was chosen to be used for column tests because it was more economical.

The results obtained at a soil to solution ratio of 2:10 points again to the possibility that the blocking of the pores assumption is correct. The increase in the amount of the soil

increased the uptake of Arsenic by Fe 1.08-Peat which could have happened because there were enough available unblocked sites for Arsenic adsorption. However, Fe 1.08-Peat had an almost similar adsorption capacity to that of Fe 0.54-Peat which was chosen to be used in column tests.

The results for the blank test confirmed that the Fe impregnation process was a source of Arsenic and that the 0.54M impregnated peat (see the bolded value in the eighth column of Table 4.6) was the best adsorbent among the treated peats. Arsenic was not the only element tested while analyzing the treated samples, however, no significant correlations were found between Arsenic levels and other elements and metal concentrations in the treated solution for the batch test.

4.3.3 Comparison Between the Arsenic Test Kit and ICP-MS Results for Batch Tests

Table 4.7 shows the difference between the results obtained by the two means. Using the As test kit is not the best option when accurate results are required. Moreover, the dilutions that were made affected the results as well. Moreover, the bubbling problem was another obstruction for obtaining results for the undiluted samples.

Table 4.7 Comparison between the Arsenic test Kit and ICP-MS Results for Batch Test

Sample tested	As Kit results in ppb	ICP-Ms results in ppb
Effluent after treating with untreated peat	Bubbles were produced which kept increasing till reaching the pad	62.61
Effluent after treating with Fe 1.08-Peat	Part of the sample was spilled. The amount left was not enough for obtaining decent results	51.69
Effluent after treating with Fe 0.54-Peat	Less than 10.86 ppb	64.02
Effluent after treating with Fe 0.108-Peat	Less than 10.86 ppb	67.89
Effluent after treating with Fe 0.054-Peat	Less than 11.2 ppb	29.84

The Arsenic test kit results were not accurate as much less Arsenic was detected than was present in the samples. The Arsenic test kit was therefore not used any further and the rest of the results were obtained only from ICP-MS analysis. Dilution errors might have been a factor, yet the error is much more than the 5-10 % that can result due to dilution errors. Measuring more control samples of different arsenic levels and predetermined arsenic concentrations by both La Motte test kit and ICP-MS would have shown how accurate both methods are as well as their disadvantages.

4.4 Column Test Results

The column tests were conducted not only because they simulate the behavior of soil to contaminated water passing through it (Yong et al., 1992) but they also test the adsorption capacity of Fe-Peat for Arsenic in a continuous flow system so that peat can be used as a filtering material.

4.4.1 Column Test for Untreated Peat

The Arsenic concentration in a 1 liter distilled water sample was spiked to 62.9 ppb and passed through untreated peat, which was compacted in the column shown in Figure 3.2 It took 108 hours for the liter to pass through. The concentration of elements that were present in the column effluent and these having significant correlations with Arsenic are tabulated below in Table 4.8.

Table 4.8 Concentration of elements in the effluent of the untreated peat column

Time/ correlation	Blank test results	Column Test spiked with As results					
	As	As	Ti	Ba	Mg	Al	Ca 43
Unit	µg/l	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l
Initial solution	7.84	62.9	1.18	1.17	0.01	0.03	0.79
12 hr	4.29	2.65	14.9	33.0	1.45	0.93	1.02
24 hr	4.32	16.2	21.7	22.2	0.99	1.03	0.81
36 hr	4.34	31.0	26.3	19.2	0.64	0.94	0.81
48 hr		32.9	26.2	16.7	0.52	0.76	0.79
60 hr	5.93	35.5	25.6	14.7	0.46	0.70	0.79
72 hr		38.8	21.2	12.3	0.38	0.51	0.80
84 hr	6.44	41.2	22.6	12.6	0.36	0.43	0.80
96 hr		42.0	23.7	12.3	0.37	0.60	0.80
108 hr	6.19	42.6	25.4	8.93	0.40	0.52	0.80
Correlation with As		1	0.73	-0.97	- 0.99	-0.80	-0.81

The results show that the untreated peat had a very low capacity for Arsenic adsorption. It reduced the Arsenic concentration from 62.86 to 2.65 μg/l in the first 12 hours then the uptake rate decreased gradually. After 108 hours, the Arsenic concentration in the column effluent went up to 42.64 μg/l. The breakthrough occurred after 36 hours where a value of 31.01 μg/l was obtained. When using Minitab, different elements' concentrations were found to be significantly correlated with the Arsenic levels such as Mg, Ca, Al, Ti, and Ba. The correlation values are shown at the bottom of Table 4.8. Most of the correlations are negatively correlated with Arsenic except for Ti. According to Vincent (1995), for data of 9 different samples, a significant correlation should be of value 0.666 or more.

It was believed that the correlations in this case did not have any indication. The Arsenic uptake started gradually to decrease because of the peat exhaustion and this is why the Arsenic concentration in the effluent kept raising. On the other hand the leaching of the other elements kept decreasing with time and the decrease was very slight approaching the 108 hours except for Ti. The correlation between Ti and As was positive, however, the values of Ti levels were almost the same after 24 hours until 108 hours. The difference between the two readings was only 0.04 ppb.

The blank column test was carried out for the untreated peat to check the level of Arsenic. The test was carried out only for 108 hours which is the same duration that the untreated peat test was carried out for. The influent was distilled water having an Arsenic concentration of 7.84 μg/l which is a very high concentration when compared to the analyzed distilled water samples from the Earth Science department which had a concentration of range 0.7 to 2 μg/l. To obtain more accurate results for the blank column test, it is recommended to use pure distilled water for future research. On the other hand, the Arsenic level for the effluent was almost constant for the first 36 hours and had a value around 4.3 μg/l. After that the concentration of Arsenic increased to 5.93 then it was almost stable around a value of 6.19 μg/l. The results of the blank test are shown in the second column of Table 4.8.

Another sample from the distilled water was examined using the ICP-MS and it was found that it had Arsenic concentration of 4.26 μg/l. The difference in Arsenic concentration between the effluent and the initial solution running into the column (influent) was very small and running more distilled water through the column would not be enough to show any trend for exhaustion especially if the other water samples to be used as influent had a very low Arsenic concentration as the second sample.

4.4.2 Column Test for Fe 0.54-Peat

For carrying out the column test using Fe 0.54-Peat as a substrate, 300 g of peat was impregnated with 0.54 M $FeCl_2$. The soil was placed and compressed into the confining cylinder of the column (see Figure 3.2) right after the soil was washed after impregnation to remove the unbounded Fe. An arsenic sample was prepared by spiking the level of Arsenic in distilled water to 64 μg/l to be used as influent. The effluent collected from the column for the first 5 hours was discarded since it was mixed with distilled water from washing the soil, which would not give the right indication for Arsenic concentration of the effluent.

The ICP-MS results for the column effluent are shown in Table 4.9 which is divided into three sections. The first section includes the first 72 hours of Arsenic adsorption and between 60 and 66 hours the Arsenic concentration in the effluent went above 10 μg/l. The second section includes from the 72^{nd} hour to the 168^{th} hour of adsorption. When the Arsenic concentration increased in the effluent, the peat was compacted so that the height of the peat in the column was reduced by 0.65 cm to increase the residence time between the Arsenic solution and Fe 0.54-Peat to reduce the Arsenic in the effluent. The peat was further compacted by applying more force on the peat surface inside the confining cylinder. This was done because it was believed that Fe 0.54-Peat was not yet exhausted. The third section includes from the 168^{th} to the 288^{th} hour of Arsenic adsorption. For further increase in the residence time, the Fe 0.54-Peat was allowed to air dry within the

column and it was compacted again after 168 hours reducing the height of peat in the column by another 0.8 cm.

Table 4.9 Concentrations of elements in the effluent of the Fe 0.54-Peat column

Time	Initial As conc.	As	pH	Fe54	Fe56	Fe57	Mg	Al	Ca43	Mn	Cu	Br	Pb
Unit	µg/l	µg/l		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
2 hr	64	39	3.4	169	29.0	283	14.2	0.42	18.3	0.38	14.7	0.62	5.2
4 hr		35	3.6	209	28.5	344	13.6	0.33	17.4	0.39	12.0	0.72	3.4
6 hr		28	3.7	234	26.5	393	10.4	0.24	14.0	0.32	8.61	0.73	2.01
8 hr		17	4	208	26.1	224	6.91	0.20	9.26	0.23	6.30	0.54	1.57
10 hr		12	4.1	163	22.2	279	4.62	0.16	6.11	0.15	6.41	0.38	1.47
12 hr		11	4.3	150	20.7	157	3.89	0.20	5.03	0.13	5.49	0.32	1.56
14 hr		7	4.5	98.1	21.9	165	2.55	0.19	3.36	0.09	3.54	0.21	1.30
16 hr		4	4.6	72.8	21.6	124	1.76	0.19	2.29	0.06	4.16	0.15	1.71
18 hr		4	4.6	66.8	21.4	114	1.49	0.11	2.19	0.06	4.97	0.13	1.78
24 hr	63	7	4.1	135	14.0	144	1.22	0.16	1.35	0.05	8.63	0.32	1.21
30 hr		7	4.5	46.6	14.4	88.1	0.32	0.10	0.43	0.01	3.74	0.05	1.04
36 hr	59	4	4.3	56.4	15.2	56.6	0.23	0.10	0.29	0.01	2.82	25	0.84
42 hr		2	4.2	37.9	14.4	38.0	0.17	0.09	0.22	0.01	2.18	0.01	0.55
48 hr	61	3	4.5	30.7	13.8	30.8	0.14	0.09	0.16	0.01	2.10	0.01	0.50
54 hrs		0	4.3	22.7	11.7	22.9	0.11	0.08	0.22	0.01	2.00	0.01	0.41
60 hr	61	3	4.6	34.9	13.1	34.9	0.45	0.08	0.38	0.01	4.82	0.06	0.60
66 hr		37	4.9	59.7	30.3	60.2	1.42	0.08	1.08	0.03	6.37	0.15	0.42
72 hr		16	4.5	24.7	12.4	24.6	0.61	0.03	0.48	0.02	2.70	0.05	0.29
First compaction													
96 hr	35	0.61	4.2	16.6	7.18	16.4	0.41	0.05	1.81	0.04	2.9	0.00	0.03
120 hr		2.92	4.2	25.1	7.22	25.0	0.45	0.08	1.82	0.03	2.5	0.00	0.02
144 hr	51	4.93	4.1	22.7	7.50	22.6	0.31	0.09	1.81	0.02	3.22	0.00	0.02
168 hr	64	2.95	4.3	15.5	7.21	15.5	0.22	0.09	0.42	0.01	1.14	0.00	0.02
Second compaction													
192 hr	56	2.32	4.7	4.7	2.23	4.72	0.64	0.03	0.47	0.01	3.43	0.00	0.07
216 hr		3.08	4.7	9.5	4.44	9.51	0.25	0.01	0.42	0.01	4.56	0.00	0.09
240 hr		3.32	4.5	16.8	7.87	16.8	0.24	0.04	0.42	0.01	5.20	0.00	0.06
264	67	3.33	4.6	19.6	9.22	19.5	0.21	0.05	0.42	0.01	4.80	0.00	0.04
288		5.78	4.7	20.1	9.50	20.0	0.17	0.06	0.42	0.01	3.49	0.01	0.03

After 14 hours, when the pH exceeded 4.3 the Arsenic concentration dropped to 7 μg/l. In the first 72 hours around four liters out of five were treated with peat to a value below 10 μg/l. The first liter took 18 hours to go through while the second to the fifth liters took 12 hours which is a very short contact time between water and soil. After compacting the peat at 72 hours, the Arsenic level dropped again to 0.61 μg/l and another 5 liters were passed through the column during which time the maximum Arsenic concentration reached 5.78 μg/l and did not exceed the 10 μg/l limit set by EPA and Canadian Environmental Quality Guidelines for Arsenic level in drinking water. The first compaction increased the residence time to 48 hours per liter then it dropped again to 24 hours per liter while the second compaction that followed the air drying increased the residence time to 72 hours. Unlike many other types of soil, it is preferable to compact peat without adding any water and after drying to obtain more compaction since peat has the ability to soak water. The drying test showed that water represents 80 % of the weight of peat. Minitab was used to find correlations between pH, Arsenic concentration and other elements' concentrations, and these results are shown in Table 4.10.

Table 4.10 Correlation between pH, Arsenic and other elements concentrations in column effluent before compaction at the first 72 hours.

Element or Metal	Correlation with pH	Correlation with As
As	- 0.52	1.000
Mg	- 0.875	0.786
Al	- 0.82	0.637
Ca 43	- 0.883	0.765
Fe 54	- 0.792	0.597
Mn	- 0.876	0.756
Fe 56	- 0.436	0.816
Fe 57	- 0.802	0.622
Cu	- 0.755	0.794
Br	- 0.840	0.728
Pb	- 0.781	0.626

The significant value to be considered in this case is 0.468 or more (Vincent, 1995). All metals were negatively correlated with pH. Cations release decreased with the increase in

pH because the net surface charge on the peat was negative above pH 3. At pH 3 (pH_{pzc}) the surface net charges are neutral then gradually with the increase in pH the negative charges dominate and start attracting positive ions. This is why the release of cations into the column effluent decreased.

It was believed in the beginning of the research that a pH below PZC would have increased Arsenic adsorption onto the positive surface due to ion exchange in addition to the formation inner sphere complexes between Arsenic and adsorbed iron hydroxide and oxyhydroxide. However, it appears from these results that Arsenic uptake depended on complexation between Arsenic and Fe and co-adsorption of Arsenic (anion) and Fe as well as the other metals (cations) onto the peat surface to maintain surface neutrality, which occurred when the Fe adsorbed to the peat became more stable at higher pH levels. The positive correlation between Fe and Arsenic and the negative correlations between pH and Arsenic, pH and Fe, and pH and the other cations indicate that the main factor for Arsenic uptake was pH. The increase in the pH in both the column and the blank tests shifted the peat surface from negative to neutral to partially positive then to positive (see Figure 2.4). This shift in peat charges stabilized the impregnated iron which attracted the Arsenic. The results shows that Fe-peat can be used for treating the contaminated water sources in Newfoundland since the pH of Newfoundland's water samples analyzed ranged between 5.1 to 9.3, accordingly, no pH adjustment will be required for treatment of these sources since the pH increase increased the Arsenic uptake during the laboratory tests.

4.4.3 Acid Digestion for the Fe 0.54-Peat After the Column Test with Spiked Arsenic Influent

After the column test was ended at 288 hours, three samples were taken from the top, middle and bottom of the column for acid digestion. The Fe and Arsenic contents of the three samples are shown below in Table 4.11

Table 4.11 Acid digestion of Fe 0.54-Peat samples after the column test with spiked As influent

	Metal Content of peat soil samples			
Fe 0.54-Peat	Fe 54 (g/kg)	Fe 57 (g/kg)	Average Fe (g/kg)	As (mg/kg)
Top column sample	127	118	123	4.39
Middle column sample	117	107	112	2.03
Bottom column sample	127	121	124	0.61

Table 4.11 shows that the Fe content in the Fe 0.54-peat decreased, which happened due to leaching of Fe during the column test. Before the column test the average Fe content was 136 g/kg while the Arsenic content was 0.5×10^{-3} g/kg (see Table 4.3). After 288 hours of Arsenic adsorption, the Arsenic content increased by 0.11×10^{-3} g/kg for the bottom soil, by 4 times for the middle soil and by almost 9 times for the top soil. The variation in the Arsenic content with depth shows that the Fe 0.54-Peat was not exhausted

yet. The top soil was adsorbing and retaining most of the Arsenic before the solution reached the bottom soil.

4.4.4 Blank Column Test for Fe 0.54-Peat

A blank column test was conducted on the Fe 0.54-Peat and the sample was compacted after 42 hours and dried then compacted again after 144 hours. The behavior of the Fe 0.54-Peat in the blank test after drying was different from that of the column test spiked with Arsenic. After drying, the Arsenic level went up then with time and with the increase in pH it went down again. The results of the blank test are shown in Table 4.12.

Table 4.12 Concentrations of elements in the effluent of blank column test of Fe 0.54-Peat.

Time	As	pH	Cr 53	Co	Mg	Si	Ca 43	Mn	Cu	Zn	Br	Pb
	µg/l		µg/l	µg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Initial Influent	7	5.8	93	182	13.5	1.10	21.7	3.99	4.62	1.10	0.98	4.99
2 hrs	171	3	205	152	11.9	0.85	28.6	9.93	10.9	2.28	1.25	9.58
4 hrs	150	3.1	205	162	25.2	0.91	29.6	10.8	18.8	2.57	1.45	10.3
6 hrs	155	3.1	213	195	13.6	1.13	33.2	11.2	16.6	2.28	1.67	11.9
8 hrs	159	3.2	214	221	14.7	1.30	36.3	11.0	17.6	2.41	1.81	11.0
10 hrs	164	3.2	223	250	15.5	1.48	39.8	10.8	18.6	2.92	2.02	11.4
12 hrs	175	3.3	232	288	14.9	1.57	43.7	10.7	15.4	2.32	2.03	9.56
14 hrs	163	3.3	212	296	13.6	1.44	42.0	9.35	12.1	1.88	1.83	7.98
16 hrs	149	3.4	188	296	12.0	1.29	38.6	7.80	9.89	1.69	1.62	7.02
18 hrs	141	3.4	165	292	20.3	1.29	35.1	6.57	8.23	1.52	1.43	6.33
24 hrs.	175	3.6	93	182	13.5	1.10	21.7	3.99	4.62	1.10	0.98	4.99
30 hrs.	86	4.0	36	69	5.8	0.83	8.95	3.32	1.99	0.74	0.55	4.59
36 hrs.	31	4.3	10	22	1.9	0.63	2.74	1.02	0.53	0.38	0.31	4.73
42 hrs.	9	4.6	3	7	0.77	0.56	0.09	0.31	0.13	144	0.20	5.16
66 hrs	1.39	4.4	24.2	1.9	0.12	0.32	0.13	0.11	1.49	0.45	0.18	0.71
96 hrs	1.45	4.3	39.1	4.8	0.19	0.46	0.26	0.20	1.81	0.77	0.18	0.96
120 hrs	2.03	4.5	71.17	10.4	0.66	0.68	1.11	0.68	5.76	1.75	0.18	0.66
144 hrs	1.47	4.6	54.38	7.5	0.63	0.75	0.57	0.44	2.44	2.76	0.18	0.25
168 hrs	5.63	4.6	1.24	2	0.14	0.35	0.43	0.08	1.64	0.48	0.02	0.71
192 hrs	4.65	4.7	1.20	1.5	0.11	0.37	0.42	0.06	1.36	0.49	0.02	0.58
216 hrs	3.69	4.7	1.37	1.2	0.07	0.25	0.42	0.04	1.21	0.40	0.02	0.35
240 hrs	3.22	4.9	2.64	1.1	0.06	0.25	0.42	0.04	1.12	0.40	0.01	0.31
264 hrs	1.96	4.9	1.48	0.9	0.06	0.24	0.42	0.04	0.94	0.31	0.01	0.25
288 hrs	1.34	5.0	1.21	0.8	0.06	0.23	0.42	0.03	0.81	0.29	0.01	0.16

The same behavior was observed for the column test with spiked Arsenic before compaction. The Fe 0.54-Peat took a longer time to start adsorbing Arsenic in the blank test compared to the column test with spiked Arsenic, however, both Fe-Peat soils reduced the Arsenic concentration. For the blank test, the Fe 0.54-Peat soil sample acted as a source of Arsenic increasing its concentration in the column effluent from 7 to 171 µg/l. The concentration of Arsenic started noticeably to decrease after 24 hours. The Arsenic level decreased to 9 µg/l after 42 hours after the pH level crossed below 10µg/l after crossing pH 4.3. This shows again that the adsorption was pH dependent. The increase in the pH could be due to the gradual shift in conditions from oxidizing to reducing and the release of OH^- groups, attached to iron hydroxide and oxyhydroxide, after it was replaced by arsenate (see Figure 2.5). The correlations of Arsenic, pH and other elements before compaction at 42 hours are presented in Table 4.13.

Table 4.13 The correlations between Arsenic, pH and other elements in the effluent of the blank column test before compacting Fe 0.54 Peat during the blank test.

Parameters	As	pH
pH	-0.89	
Mg	0.71	-0.52
Si	0.74	-0.47
Ca	0.84	-0.65
Cr	0.85	-0.74
Mn	0.85	-0.76
Co	0.76	-0.52
Cu	0.77	-0.72
Zn	0.82	-0.73
Br	0.84	-0.67
Pb	0.74	-0.70

Both cations and anions released to the effluent are showing negative correlations to pH increase. The cations were adsorbed due to the induced negative charges on the surface because of the pH increase, while the anions could be co-adsorbed or form inner sphere complexes with the impregnated Fe. After the compaction all the analyzed elements were showing a significant correlation with Arsenic.

4.5 Statistical Analysis Results

4.5.1 Analysis of Newfoundland Water Sources

The results obtained from the Government of Newfoundland and Labrador for Newfoundland water analysis are presented in a CD attached to the thesis for the ease of accessing the information.

4.5.2 Parameters Correlated with Arsenic in Newfoundland Water and Globally

The results obtained from the Government of Newfoundland and Labrador for the chemical analysis of Newfoundland water were statistically analyzed using Minitab to find correlations between Arsenic and other chemical parameters. This was done to determine the possible reasons for natural Arsenic release in Newfoundland. In Table 4.14 the values of significant correlations of different parameters with Arsenic are listed.

The values are arranged descendingly according to their absolute values for each region separately, as well as for all regions combined.

Table 4.14 Significant correlations of physical properties and chemical parameters with Arsenic (adapted from Rageh et al., 2007)

	Arsenic and	Pearson's Correlation (r) P-value			
		Eastern (87)	Western (25)	Central (16)	Provincial
1	Bromide	0.660			0.386
2	Hardness	0.589			0.250
3	Antimony	0.509	-0.499		0.249
4	Chloride	0.494	-0.630		
5	Sulfate	0.476	-0.670		
6	Zinc	0.474			
7	Magnesium	0.418		-0.690	0.175
8	Chromium	0.407			0.308
9	Calcium	0.381	-0.442		
10	Color	0.377	0.634	0.689	0.504
11	Total Divalent ions	0.372	-0.423		
12	Total Dissolved solids	0.355	-0.728	-0.532	-0.159
13	Cadmium	0.352			
14	Conductivity	0.331	-0.727	-0.538	-0.174
15	Flouride	-0.322	-0.611		-0.305
16	pH level	-0.309	-0.692	-0.661	-0.403
17	Aluminum	-0.301	0.514		0.249
18	Potassium	-0.264	-0.769	-0.678	-0.313
19	Sodium	0.242	-0.616	-0.568	
20	Alkalinity	-0.192	-0.769	-0.776	-0.423
21	Lead		0.415		
22	Total Phosphorus		-0.567		

There are many countries suffering from Arsenic contaminated drinking water. The Arsenic problem in these affected regions was mostly correlated to reducing conditions. It has been documented as well that the Arsenic level was increasing in groundwater year after year with the shifting towards more reducing conditions in Bengal Delta Plain in India (Wagner et al., 2005). The reasons for reducing conditions in this region were anthropogenic such as agricultural practices, fertilizer use and sewage percolation to groundwater, which increased the amount of substrate available for microorganisms increasing their oxygen consumption (Chandrasekharam, 2005; Wagner et al., 2005). The positive correlation between the HCO_3^- content and Arsenic levels indicated microbial degradation of organic matter which contributed to reducing conditions (Sikder and Khan, 2005; Tandukar, 2005). In Nepal, the Arsenic presence was correlated to the presence of organic carbon, iron and manganese presence as well (Tandukar, 2005).

The reducing conditions enhanced the reductive dissolution of Arsenic bearing minerals such as sulfates, iron oxides, iron oxyhydroxides and manganese (Wagner et al., 2006). Arsenic levels in groundwater in India, Bangladesh and Nepal were found to be correlated with sulfates, iron and manganese which totally supports the theory of reductive dissolution of Arsenic bearing minerals (Ohno et al., 2005; Anawara et al., 2003, Sikder and Khan, 2005; Tandukar, 2005). Another hypothesis for Arsenic removal is that the over use of groundwater has caused the reduction in the groundwater level subjecting sediments and minerals of aquifers above the groundwater Table to more oxygen and causing Arsenic release. However, the oxidation of Arsenic bearing minerals above the groundwater Table hypothesis does not explain the higher concentration of

Arsenic at depths ranging from 12 to 35 m below the water Table and the dominance of As (III) over As (V) in the Bengal Delta Plain in India (Wagner et al., 2005). If the oxidation theory was true, Arsenic should have been present in the As (V) form and it would have the highest concentration closer to the ground surface.

There are many other studies on the Arsenic problem in other countries such as Vietnam, Mongolia and some parts of Argentina and the United States. In most of the affected regions of these countries, the conditions were reducing and/or alkaline. The dominant species was As (III) which is very mobile and toxic. The presence of Arsenic in these countries was correlated to high pH as Arsenic tends to desorb under alkaline conditions. Arsenic was also correlated with oxides such as iron, aluminum and/or manganese oxides and the responsible mechanism of Arsenic release was believed to be reductive dissolution (Rageh et al., 2007). In Table 4.15 different parameters were found to be correlated with Arsenic in different regions of the world.

Table 4.15 Parameters correlated with Arsenic in drinking water in different regions and countries (adapted from Rageh et al., 2007)

(r)	Ions and Parameters	Regions
-ve	SO_4^{2-}	Bangladesh (Nawabganj)
+ve	Fe, Mn, & Al	Bangladesh U.S. (Florida)
+ve	pH	Argentina, U.S., India, Botswana Bangladesh
+ve	Alkalinity	Areas in Bangladesh, U.S., Argentina
+ve	Dissolved organic carbon (DOC)	Bangladesh,
+ve	NH_4^+	Bangladesh

In contrast, of the samples from water sources in Newfoundland that were analyzed, it was found that 37 were alkaline, and 15 were acidic. Arsenic correlations with Mn, Fe, Al, HCO_3 were insignificant and the Arsenic concentration was negatively correlated with pH. Arsenic was found to be positively correlated with SO_4^{2-}, yet in the central and western part of Newfoundland the correlation was negative. The groundwater conditions

were oxidizing, the dominant Arsenic species was As (V), and reductive dissolution was not believed to be the reason for Arsenic dissolution especially in the eastern region. Oxidation of sulfide bearing minerals by water from heavy precipitation all over the year may be the mechanism responsible for Arsenic release especially in the eastern region where concentrations of both sulfate and Arsenic were correlated, and the sulfate concentration was high (4-50 mg/l). Rainfall might also be responsible for the presence of other salts. Rainfall may cause entrained salts carried by wind from the sea, such as Cl and Br, to dissolve and fall with precipitation. During percolation of rainfall, other metals and ions can be dissolved and leached by the infiltrating water till reaching the groundwater (Rageh et al., 2007).

Iron is a component of one of the Arsenic bearing minerals, arsenopyrite (FeAsS), in Newfoundland, yet its concentration in drinking water sources was very low. This is because under oxidizing conditions soluble and solid Fe^{2+} will be oxidized to Fe^{3+} which will tend to adsorb rather than desorb Arsenic. Accordingly, arsenopyrite (FeAsS) cannot be a source of Arsenic in water under oxidizing conditions, however, other sulfide minerals might be responsible for Arsenic release (Rageh et al., 2007). The Arsenic problem in the Czech republic was believed to be due to different mechanisms. Arsenic mobilization to water was due to mining activities. Oxidation of arsenopyrite (FeAsS) caused the release of dissolved Fe and Arsenic. After the mine was closed in 1991, floods together with the prevailing reducing conditions caused the dissolution of Fe and Arsenic and their presence in high concentrations in mine water at Kank (Kopriva et al., 2005).

In alluvial aquifers in the Santiego del Estro province , Argentina, the conditions were similar to those in Newfoundland. The groundwater pH in Argentina ranged between 6.4 and 9.3 with an average of 7.6 and the dominant species was As (V). The conditions were oxidizing and dissolved organic carbon (DOC) was having a low concentration. The Al concentrations low and Fe and Mn were around 0.5 mg/l. However, the Arsenic concentration was very high in some areas reaching up to14 mg/l. High pH values were believed to be the reason for the high Arsenic concentration. The dissolution of Arsenic from volcanic rocks was not the main reason for the high Arsenic levels since the Arsenic dissolution was followed by Arsenic adsorption onto the surfaces of the released Al, Fe and Mn into the groundwater. However, Arsenic was desorbed again due to high pH levels (Bundschuh et al., 2005). In Newfoundland the pH of the analyzed samples ranged between 5.1 and 9.3 with an average of 7.6, however, the Arsenic concentration was found to be negatively correlated with pH levels. The Arsenic concentration was not as high. The maximum concentration was 44 μg/l, the minimum was 10 μg/l and the average was 16.7 μg/l.

The reason for Arsenic release might be the oxidation of minerals bearing both Arsenic and sulfide which could have been the reason for the co-presence of both Arsenic and sulfates. Such co-existence may have contributed to the high Arsenic concentration as both compete for the same sites of adsorption on solid surfaces. The presence of Sb in groundwater was also positively correlated with Arsenic in the eastern region and both elements belong to the same column of the periodic Table. They both have similar properties and compete for similar sites on solid surfaces which might be another reason

for the positive correlation between Arsenic and Sb (Katsoyiannis and Katsoyiannis, 2006; Rageh et al., 2007).

Principal component analysis results showed similarities in both physical and chemical properties between wells located in the same region for the three regions and especially for the eastern region. That might be due to the fact that each region has a different geology. Samples from sources in the east were taken from areas located within sandstone formations while those from the west and central Newfoundland were taken from areas with more volcanic and metamorphic rocks and fewer limestone and sandstone formations. The concentration of Arsenic bound to different geological formations was not found to be correlated with the Arsenic concentration in the water. Sandstone and shale have higher Arsenic concentrations than volcanic and metamorphic rocks, however, there were areas with higher Arsenic concentrations located within the latter formations than those located in the former. Geological formations might be a reason for Arsenic presence in water sources but not the main factor in the Arsenic release equation (Rageh et al., 2007).

Chapter Five

Conclusions and recommendations

5.1 Conclusion

This study was concerned with the removal of Arsenic from drinking water. Most of the work was laboratory based and did not include any field experiments. However, field data on different water sources in Newfoundland was obtained from the Government of Newfoundland and Labrador for the statistical analysis. The concentration of Arsenic in the spiked distilled water samples prepared for the column tests with Arsenic was around 60 µg/l, while the max concentration in the analyzed samples of Newfoundland water sources was 44 µg/l (Guzzwell, 2006).

The experimental work started with three characterization tests, PZC, CEC and acid digestion to determine the characteristics and Arsenic and Fe contents of the peat. The characteristics of peat were studied both before and after impregnation for the untreated peat and the four Fe-Peat soils. It was found that the PZC increased by 1, 0.9, 1, and 1.3 pH units for Fe 0.054-Peat, Fe 0.108-Peat, Fe 0.54-Peat, and Fe 1.08-Peat respectively after impregnation._The values of the CEC of the treated peat soils were negatively correlated with the concentration of the Fe in the impregnation solutions. The more the Fe in the impregnation solution for treating the peat the less the CEC of the treated peat.

Acid digestion results showed that peat soils treated with 0.054 M and 0.108 M impregnation solutions were having almost the same Fe content. Both the 0.54 M and the 1.08 M impregnation solutions increased the Fe content of peat by two times compared to Fe 0.054-Peat and Fe 0.108-Peat. The dry weight test showed that water represented 80 % of the peat content by weight.

The behavior of the four Fe-peats was not clear enough during the batch tests. The potential of Fe-peat to remove Arsenic varied with the change in the soil to solution ratio. For the soil to solution ratio of 1:10 and the blank test, Fe 0.54-Peat showed the best adsorption capacity among the impregnated soils. However, for the 2:10 ratio, the Arsenic level in effluent reached its lowest concentration in the solutions tested with the untreated peat (see Figure 4.6). This was because the Fe-peat was a source of arsenic itself. The $FeCl_2$ that was used for impregnation had an Arsenic concentration of 10 μg/g, which started leaching and this was the reason for having a higher Arsenic level for the

effluent from the 0.054-Peat and Fe 0.108-Peat than that in the spiked initial solution. Moreover, As concentration in the initial solution was much more than these mentioned in the initial condition row in Table 4.6 and accordingly the quantity of arsenic removed by peat is much more than the quantity that can be calculated from Table 4.6 (by subtracting the As concentration of the effluent from the arsenic concentration of the initial solution). However, the aim of the batch test was to experiment the ability of impregnated peat soils to retain their arsenic content and to lower the arsenic content of an initial solution of arsenic concentration ranging around 60 μg/l. This was done to pick up the best adsorbant for further experimentation using column test.

For Fe-Peat soils, the Arsenic uptake was positively correlated to the Fe concentration in the impregnating solution except for the Fe 1.08-Peat, which showed less adsorption capacity (44.7, 88.4, 138 μg/l left in the effluent after treatment) than the Fe 0.54-Peat (29.8, 90.1, 32.9 left in the effluent after treatment) (see Figure 4.6). This could be due to the high concentration of Fe (1.08 M) that was used during impregnation which caused the blocking of the pores of peat, which later prevented Arsenic from diffusing into these pores resulting in less adsorption.

The results obtained from the batch experiments showed that the increase in pH was associated with an increase in Arsenic uptake. Fe 0.54-Peat was capable of reducing the Arsenic concentration to half the original value for the 1:10 soil to solution ratio batch experiment and it showed the best adsorption capacity among the other Fe-Peat soils, and that was why it was used in column tests.

The objective of the research was to find a cheap material to be used as a substrate for removing Arsenic in a continuous flow system so that it could be used as a filter material. For this purpose, the column test was conducted. Untreated peat reduced the Arsenic concentration from 62.86 μg/l in the influent to 2.65 μg/l in the effluent in the first 12 hours. However, the peat got exhausted and the Arsenic concentration increased to 16.19 μg/l and kept building up in the effluent gradually till reaching breakthrough (31.01 μg/l) after 36 hours.

The Fe 0.54-Peat reduced the Arsenic level of the prepared solution gradually till it reached 7 μg/l after 14 hours and after the pH went over 4.3. Despite the short contact time between Arsenic and Fe 0.54-Peat, which was 18 hours for the first liter and 12 hours for each of the second to the fifth liters to pass through the column, the Arsenic concentration was less then 10 μg/l and most of the time it was less than 5 μg/l. The peat was able to treat 4 liters of Arsenic to a level below the limit set by the U.S.EPA and Canadian Environmental Quality Guidelines till it went up suddenly to 37 μg/l after 66 hours. Accordingly, after this the Fe 0.54-Peat was further compacted twice, after 72 hours and 168 hours, since the sudden increase appeared to be due to an inadequate contact between the adsorbate and the adsorbent rather than an exhaustion of the substrate.

After the first compaction at 72 hours the concentration of Arsenic in the effluent dropped to 0.61 μg/l and it did not exceed 5.78 μg/l while another five liters were passed

through the column. The contact time was increased to 48 hours for the sixth liter, or the first liter after the first compaction, to pass through the column then dropped to 24 hours for the seventh and the eight liters. After the second compaction at 168 hours, the time for the ninth and tenth liters to pass through the column increased again to 72 hours.

The blank column test followed a different trend. The Arsenic concentration went up from 7 μg/l in the influent blank solution to 171 μg/l in the effluent after 2 hours and the Arsenic concentration kept going up and down till it was reduced to 86 μg/l after 30 hours at pH 4 then 31 μg/l after 36 hours at pH 4.3. After crossing this pH value, the Arsenic concentration went down to 9 μg/l which is below the 10 μg/l limit for drinking water. The Arsenic level kept going up and down even after compaction and it did not exceed the allowable limit until the end of the test at 288 hours. The test was ended after 288 hours due to time constraints and it has nothing to do with the peat exhaustion and the acid digestion carried out for the soil samples of the column test with spiked Arsenic influent proved that the peat had not yet been saturated.

The results showed that the pH was the main factor affecting the Arsenic uptake. The pH was also highly correlated with the Fe and other cations retention on peat, which points towards two different mechanisms for Arsenic uptake. The first is the formation of inner sphere complexes between Arsenic and Fe which formed covalent bonds with the functional groups of peat as illustrated in Figures 2.2, 2.3, 2.4 and 2.5 . When the pH increased, the surface charges of peat became negative retaining and stabilizing the impregnated Fe, reducing Fe leaching into the column effluent, and attracting Arsenic

anions. The Fe adsorbed on the surface led to the uptake of more Arsenic to neutralize the positive charges of Fe, due probably to a combination of ion exchange and complexation which is the second mechanism involved. This kind of adsorption has been documented before by Brown et al. (1999).

The statistical analysis showed that the eastern region sources had many similarities in both physical and chemical properties. Each of the three regions was different from the other two but were having some similarities in their water sources. This could be due to the different geological formations of each region. The reason for the Arsenic release is believed to be due to the oxidation of Arsenic bearing formations induced by heavy precipitation all year round.

Rainfall could be the reason for the presence of elements such as Br and Cl in ground water and their correlation with Arsenic. Salts of Br and Cl entrained by the air from the ocean could dissolve and fall in the form of wet precipitation that percolates and oxidizes Arsenic carrying Br, Cl, As, and all the other weathered elements to groundwater (Rageh et al., 2007).

5.2 Recommendations

For obtaining better compaction results and a higher contact time during the column tests, peat could be air dried and wet compaction could be avoided. This is because peat has a high potential for absorbing water, swelling, and retaining water. The dry weight test

showed that water represented 80 % of the weight of the peat. When the Fe 0.54-Peat was air dried and compacted at 168 hours, 1.4 cm of soil settlement was obtained. For obtaining more accurate results for blank tests, a source of free arsenic distilled water is preferred. $FeCl_2$ that was used for impregnating peat in this study had an arsenic concentration of 10 μg/l which made impregnated peat itself a source of arsenic. Therefore, it is recommended for future research to monitor the release of arsenic from iron impregnated peat separately before starting the adsorption tests to account for the increase in arsenic concentration in the solution to be treated. It will also be of great importance if future studies include calculations for peat saturation with arsenic.

When working within a very small range at very low concentrations, it is important to use a reliable and U.S.EPA approved method such as ICP-MS. The ICP-MS Hewlett-Packard 4500 that was used in this study was a sensitive technique that provided an accurate measure for Arsenic levels at concentrations as low as 1 μg/l. Sometimes methods such as Arsenic test kits can be helpful on site for obtaining instant Arsenic readings, however, the La Motte test kit that was used here was not suiTable for measuring Arsenic. In addition, extra samples should be prepared and kept in case of errors. Two Test kit measurements of Arsenic level were not obtained in this study due to spillage and other errors.

5.3 Future Research

The results obtained from this research show that Fe-Peat could be a cheap and effective material for treating Arsenic. However, more research is required to know the main factors affecting the Arsenic uptake and the parameters controlling the impregnation process. Moreover, there are some questions about the possibility of controlling the pH of the soil such that a pH 4.3 can be reached instantly without leaching of impregnated peat and maladsorption of Arsenic till the pH of the effluent reaches this value. To obtain more information about Arsenic release into water sources in Newfoundland, more monitoring is required and more samples should be collected at different times of the year. This would help in detecting the seasonal effect on Arsenic release and would help in understanding and testing the effect of different conditions on Arsenic bearing minerals and their weathering.

Appendix

A.1 Calculations

- *For preparing the base solution:*

1 N is equal to 1 M x n (which is the number of H^+ or OH^- provided by the formula of acid). The number of OH^- is 1, Therefore, 1 M of NaOH is equivalent to 1 N of NaOH. The number of grams/mole for NaOH is 40.

0.01 N NaOH = 40g/mole x 0.01 mole/ liter = 0.04 g/ liter

For preparing the acid solution:

The same rule applies for HCl as for NaOH. 1 N HCl = 1 M HCl. The HCl used was obtained from Fisher Scientific. It has a concentration of 30 % and density of 1149 g/l at 20 °C

1 N HCl = density (g/liter) x concentration / Molecular wt

= 1149 x 0.3 / 36.48= 9.45 mole/liter

- *For dilution:*

For reaching the required concentration, 40 ml of sample was diluted. The number of moles does not change after the dilution, therefore the number of moles before dilution is equal to the number of moles after dilution:

$M_1 V_1 = M_2 V_2$

$9.45 \times 4 = 0.1 \times V_2$

$V_2 = 378$ ml

- *For getting the amount of consumed (H^+) or base (OH^-) in mequ/ g:*

For HCl and NaOH mmol = m Eq.

Therefore, M (mole/ liter) x 1000 mmole/mole x # of ml added / (1000ml/ l)

For obtaining the results in mequ/g, mmol should be divided by the wt of soil used

A.2 Permission of Author and Publisher for the Use of Tables and Figure

A.3 Tables

The first Table (Table A.1) is a spread sheet that includes chemical and physical analysis of 128 water sources in Newfoundland. It is attached on a CD for the ease of obtaining information if required.

A.3.1 Correlation of As Level with Physical Properties and Chemical Parameters of Newfoundland Water Resources

Table A.2 Provincial correlations

Correlations: ARSENIC, ALKALINITY, COLOR, CONDUCTIVITY, HARDNESS, PH_LEVEL, ...

	ARSENIC	ALKALINITY	COLOR	CONDUCTIVITY	
ALKALINITY	-0.423				
	0.000				
COLOR	0.504	-0.503			
	0.000	0.000			
CONDUCTIVITY	-0.174	0.619	-0.255		
	0.055	0.000	0.005		
HARDNESS	0.250	0.373	0.159	0.331	
	0.013	0.000	0.119	0.001	
PH_LEVEL	-0.403	0.694	-0.519	0.457	
	0.000	0.000	0.000	0.000	
TDS	-0.159	0.610	-0.246	0.999	
	0.080	0.000	0.006	0.000	
TSS	0.040	0.323	0.000	0.358	
	0.846	0.108	0.998	0.073	
TURBIDITY	-0.015	0.153	-0.018	0.097	
	0.872	0.092	0.843	0.286	
BORON	-0.123	0.422	-0.064	0.753	
	0.228	0.000	0.533	0.000	
BROMIDE	0.386	0.242	0.014	0.540	
	0.000	0.017	0.891	0.000	

CALCIUM	-0.025	0.553	-0.204	0.444
	0.780	0.000	0.025	0.000
CHLORIDE	-0.071	0.422	-0.128	0.972
	0.438	0.000	0.160	0.000
FLUORIDE	-0.305	0.422	-0.260	0.575
	0.001	0.000	0.004	0.000
POTASSIUM	-0.313	0.567	-0.138	0.767
	0.000	0.000	0.130	0.000
SODIUM	-0.146	0.466	-0.191	0.913
	0.107	0.000	0.035	0.000
SULPHATE	-0.020	0.458	-0.282	0.895
	0.827	0.000	0.002	0.000
AMMONIA	-0.086	0.234	0.047	0.146
	0.406	0.023	0.651	0.159
DOC	-0.051	0.234	0.378	0.174
	0.592	0.013	0.000	0.066
NITRATE_ITE	-0.116	-0.052	-0.224	0.021
	0.205	0.573	0.013	0.823
TOTALPHOSPHO	-0.069	0.171	-0.160	0.047
	0.449	0.060	0.078	0.605
ALUMINIUM	0.249	-0.067	0.279	0.173
	0.005	0.464	0.002	0.056
ANTIMONY	0.482	-0.099	-0.116	0.029
	0.000	0.371	0.293	0.793
BARIUM	-0.149	0.261	-0.096	0.026
	0.144	0.010	0.351	0.800
CADMIUM	0.031	0.079	-0.027	-0.021
	0.735	0.386	0.768	0.816
CHROMIUM	0.308	-0.087	0.443	0.078
	0.001	0.343	0.000	0.390
COPPER	0.023	-0.010	0.040	0.135
	0.798	0.914	0.661	0.139
IRON	-0.017	0.166	0.016	0.142
	0.854	0.068	0.864	0.118
LEAD	-0.074	0.056	-0.037	0.024
	0.410	0.542	0.688	0.796
MAGNESIUM	0.173	0.410	-0.229	0.304
	0.056	0.000	0.011	0.001
MANGANESE	-0.137	0.342	0.028	0.355
	0.130	0.000	0.756	0.000
MERCURY	-0.081	-0.002	0.246	0.020
	0.427	0.985	0.015	0.845

NICKEL	0.183	-0.153	0.227	0.015
	0.043	0.092	0.012	0.874
SELENIUM	0.060	-0.269	-0.054	-0.092
	0.560	0.008	0.601	0.370
URANIUM	0.062	-0.196	-0.096	-0.118
	0.575	0.074	0.385	0.285
ZINC	0.015	0.114	-0.023	0.044
	0.869	0.212	0.798	0.628

Table A.3 Central region correlations

Correlations: ARSENIC_1, ALKALINITY_1, COLOR_1, CONDUCTIVITY, HARDNESS_1, ...

	ARSENIC_1	ALKALINITY_1	COLOR_1	CONDUCTIVITY
ALKALINITY_1	-0.776			
	0.000			
COLOR_1	0.689	-0.546		
	0.003	0.029		
CONDUCTIVITY	-0.538	0.722	-0.267	
	0.031	0.002	0.318	
HARDNESS_1	-0.274	0.685	0.495	0.965
	0.415	0.020	0.122	0.000
PH_LEVEL_1	-0.661	0.735	-0.817	0.326
	0.005	0.001	0.000	0.218
TDS_1	-0.532	0.709	-0.253	0.999
	0.034	0.002	0.345	0.000
TSS_1	*	*	*	*
	*	*	*	*
TURBIDITY_1	0.006	0.272	-0.189	0.133
	0.982	0.308	0.484	0.623
BORON_1	0.401	-0.648	-0.646	-0.515
	0.221	0.031	0.032	0.105
BROMIDE_1	-0.101	0.391	0.302	0.356
	0.768	0.234	0.367	0.282
CALCIUM_1	-0.446	0.673	-0.179	0.973
	0.083	0.004	0.507	0.000
CHLORIDE_1	-0.413	0.567	-0.151	0.979
	0.112	0.022	0.576	0.000
FLUORIDE_1	-0.111	-0.072	-0.353	-0.309
	0.683	0.791	0.179	0.244
POTASSIUM_1	-0.678	0.792	-0.436	0.908
	0.004	0.000	0.091	0.000
SODIUM_1	-0.568	0.735	-0.316	0.955
	0.022	0.001	0.233	0.000
SULPHATE_1	-0.436	0.662	-0.151	0.934
	0.091	0.005	0.576	0.000
AMMONIA_1	-0.191	0.135	0.074	0.297
	0.573	0.693	0.830	0.375
DOC_1	-0.127	0.568	0.280	0.526
	0.666	0.034	0.332	0.053

NITRATE_ITE_	-0.450	0.678	-0.226	0.621
	0.081	0.004	0.400	0.010
TOTALPHOSPHO	0.026	0.223	-0.253	0.017
	0.922	0.407	0.345	0.951
ALUMINIUM_1	0.311	0.042	0.227	0.436
	0.241	0.877	0.397	0.092
ANTIMONY_1	0.391	-0.140	-0.326	0.080
	0.298	0.719	0.392	0.837
ARSENIC_1	1.000	-0.776	0.689	-0.538
	*	0.000	0.003	0.031
BARIUM_1	0.240	0.549	0.359	0.584
	0.476	0.080	0.278	0.059
CADMIUM_1	0.127	0.162	-0.169	-0.087
	0.638	49	0.532	0.748
CHROMIUM_1	0.094	0.233	0.189	0.255
	0.729	0.386	0.484	0.341
COPPER_1	-0.298	0.262	-0.073	0.469
	0.261	0.326	0.788	0.067
IRON_1	-0.039	0.324	-0.177	0.229
	0.887	0.221	0.511	0.393
LEAD_1	0.003	0.252	-0.175	0.118
	0.990	0.347	0.516	0.664
MAGNESIUM_1	-0.690	0.815	-0.463	0.838
	0.003	0.000	0.071	0.000
MANGANESE_1	-0.343	0.601	-0.094	0.719
	0.193	0.014	0.729	0.002
MERCURY_1	0.513	-0.137	-0.370	-0.065
	0.106	0.687	0.263	0.850
NICKEL_1	0.277	-0.235	0.013	-0.126
	0.299	0.380	0.963	0.641
SELENIUM_1	0.513	-0.137	-0.370	-0.065
	0.106	0.687	0.263	0.850
URANIUM_1	*	*	*	*
	*	*	*	*
ZINC_1	0.073	0.231	-0.181	0.032
	0.789	0.390	0.502	0.907

Table A.4 Eastern region correlations

Correlations: ARSENIC_1_1, ALKALINITY_1, COLOR_1_1, CONDUCTIVITY, ...

	ARSENIC_1_1	ALKALINITY_1	COLOR_1_1	CONDUCTIVITY
ALKALINITY_1	-0.192 0.085			
COLOR_1_1	0.377 0.001	-0.655 0.000		
CONDUCTIVITY	0.331 0.003	0.525 0.000	-0.443 0.000	
HARDNESS_1_1	0.589 0.000	0.153 0.190	-0.139 0.235	0.656 0.000
PH_LEVEL_1_1	-0.309 0.005	0.664 0.000	-0.548 0.000	0.276 0.013
TDS_1_1	0.355 0.001	0.491 0.000	-0.416 0.000	0.997 0.000
TSS_1_1	1.000 *	-0.999 0.000	0.708 0.075	-0.996 0.000
TURBIDITY_1_	-0.198 0.076	0.324 0.003	-0.007 0.948	0.112 0.320
BORON_1_1	-0.219 0.058	0.175 0.134	0.543 0.000	-0.091 0.435
BROMIDE_1_1	0.660 0.000	0.068 0.562	0.027 0.815	0.806 0.000
CALCIUM_1_1	0.381 0.000	0.460 0.000	-0.429 0.000	0.698 0.000
CHLORIDE_1_1	0.494 0.000	0.094 0.405	-0.141 0.210	0.891 0.000
FLUORIDE_1_1	-0.322 0.003	0.270 0.015	-0.266 0.016	0.005 0.963
POTASSIUM_1_	-0.264 0.017	0.196 0.079	-0.065 0.564	0.135 0.231
SODIUM_1_1	0.242 0.028	0.461 0.000	-0.260 0.019	0.662 0.000
SULPHATE_1_1	0.476 0.000	0.128 0.255	-0.283 0.011	0.803 0.000
AMMONIA_1_1	-0.069 0.557	0.152 0.193	0.156 0.180	0.102 0.383
DOC_1_1	-0.192 0.099	0.102 0.386	0.555 0.000	-0.083 0.481
NITRATE_ITE_	-0.050	-0.133	-0.185	0.199

	0.657	0.236	0.099	0.075
TOTALPHOSPHO	-0.096	0.148	-0.263	0.007
	0.396	0.187	0.018	0.954
ALUMINIUM_1_	0.301	-0.060	0.126	0.188
	0.006	0.598	0.264	0.093
ANTIMONY_1_1	0.509	0.033	-0.044	0.460
	0.000	0.794	0.725	0.000
BARIUM_1_1	-0.176	0.133	-0.040	-0.124
	0.128	0.254	0.734	0.291
CADMIUM_1_1	0.352	-0.664	0.871	-0.434
	0.001	0.000	0.000	0.000
CHROMIUM_1_1	0.407	-0.174	0.457	-0.129
	0.000	0.119	0.000	0.250
COPPER_1_1	0.054	-0.038	0.016	0.071
	0.631	0.735	0.886	0.531
IRON_1_1	-0.066	0.238	0.076	0.159
	0.556	0.032	0.498	0.156
LEAD_1_1	-0.092	-0.021	-0.022	-0.045
	0.402	0.852	0.844	0.689
MAGNESIUM_1_	0.418	0.195	-0.294	0.678
	0.000	0.081	0.008	0.000
MANGANESE_1_	-0.108	0.288	0.016	0.168
	0.336	0.009	0.889	0.134
MERCURY_1_1	0.072	0.138	0.355	0.182
	0.537	0.237	0.002	0.118
NICKEL_1_1	0.138	-0.036	0.198	0.041
	0.215	0.752	0.077	0.718
SELENIUM_1_1	0.071	-0.250	-0.126	-0.004
	0.544	0.030	0.280	0.975
URANIUM_1_1	0.053	-0.115	-0.175	0.080
	0.672	0.357	0.160	0.523
ZINC_1_1	0.474	0.059	-0.008	0.530
	0.000	0.599	0.942	0.000

Table A.5 Western region correlations

Correlations: ARSENIC_2, ALKALINITY_2, COLOR_2, CONDUCTIVITY, HARDNESS_2, ...

	ARSENIC_2	ALKALINITY_2	COLOR_2	CONDUCTIVITY
ALKALINITY_2	-0.769 0.000			
COLOR_2	0.634 0.001	-0.608 0.001		
CONDUCTIVITY	-0.727 0.000	0.684 0.000	-0.585 0.002	
HARDNESS_2	-0.251 0.457	0.420 0.198	-0.198 0.560	-0.641 0.033
PH_LEVEL_2	-0.692 0.000	0.773 0.000	-0.622 0.001	0.809 0.000
TDS_2	-0.728 0.000	0.682 0.000	-0.582 0.002	1.000 0.000
TSS_2	0.000 1.000	0.278 0.316	0.002 0.995	0.321 0.243
TURBIDITY_2	-0.019 0.929	0.385 0.057	0.108 0.609	0.114 0.587
BORON_2	-0.266 0.430	0.266 0.429	-0.566 0.069	0.969 0.000
BROMIDE_2	-0.194 0.567	0.120 0.725	-0.279 0.406	0.483 0.132
CALCIUM_2	-0.442 0.027	0.631 0.001	-0.237 0.253	-0.075 0.721
CHLORIDE_2	-0.630 0.001	0.535 0.006	-0.518 0.008	0.982 0.000
FLUORIDE_2	-0.611 0.001	0.670 0.000	-0.515 0.008	0.942 0.000
POTASSIUM_2	-0.769 0.000	0.799 0.000	-0.637 0.001	0.899 0.000
SODIUM_2	-0.616 0.001	0.519 0.008	-0.509 0.009	0.976 0.000
SULPHATE_2	-0.670 0.000	0.617 0.001	-0.562 0.003	0.985 0.000
AMMONIA_2	-0.237 0.540	0.774 0.014	-0.363 0.338	-0.512 0.159
DOC_2	-0.332	0.027	0.149	-0.342

	0.122	0.902	0.499	0.110
NITRATE_ITE_	0.182 0.384	-0.187 0.370	-0.061 0.771	0.124 0.554
TOTALPHOSPHO	-0.567 0.003	0.735 0.000	-0.552 0.004	0.564 0.003
ALUMINIUM_2	0.514 0.009	-0.507 0.010	0.675 0.000	-0.355 0.082
ANTIMONY_2	-0.499 0.172	-0.054 0.891	-0.346 0.362	0.816 0.007
BARIUM_2	-0.114 0.740	0.836 0.001	-0.501 0.117	-0.162 0.635
CADMIUM_2	0.012 0.954	-0.388 0.055	0.299 0.147	-0.452 0.023
CHROMIUM_2	0.041 0.844	-0.294 0.153	0.181 0.386	-0.223 0.283
COPPER_2	0.166 0.429	-0.236 0.257	-0.045 0.829	-0.148 0.480
IRON_2	0.120 0.566	0.021 0.920	0.490 0.013	-0.173 0.407
LEAD_2	0.415 0.039	-0.613 0.001	0.415 0.039	-0.183 0.382
MAGNESIUM_2	-0.251 0.226	0.563 0.003	-0.252 0.225	-0.068 0.745
MANGANESE_2	-0.388 0.055	0.606 0.001	-0.355 0.081	0.030 0.885
MERCURY_2	-0.506 0.112	-0.585 0.059	0.199 0.557	-0.362 0.274
NICKEL_2	0.083 0.692	-0.402 0.046	0.252 0.224	-0.094 0.654
SELENIUM_2	-0.562 0.072	-0.587 0.057	0.125 0.713	-0.223 0.510
URANIUM_2	* *	* *	* *	* *
ZINC_2	-0.302 0.142	0.196 0.349	-0.217 0.296	0.472 0.017

A.3.2 The Data Obtained from the PZC Experiments

Table A.6 Titration Table for determining the PZC for the untreated peat

ml of base/ acid added	mequ/g added	pH 1 M NaCl	pH 0.1 M NaCl	pH 0.01 M NaCl	pH 0.001 M NaCl
22	1.1	1.3	1.44	1.51	1.49
20	1	1.32	1.45	1.56	1.48
18	0.9	1.31	1.5	1.49	1.5
16	0.8	1.36	1.54	1.55	1.51
14	0.7	1.39	1.59	1.64	1.59
12	0.6	1.43	1.63	1.71	1.62
10	0.5	1.48	1.68	1.8	1.72
8	0.4	1.51	1.71	1.91	1.8
6	0.3	1.63	1.83	1.91	1.91
4	0.2	1.78	1.97	2.09	2.12
2	0.1	2.06	2.37	2.47	2.45
0	0	2.8	3	3.5	3.72
4	-0.02	3.12	3.36	4.06	4.62
8	-0.04	3.34	3.69	4.47	5.2
12	-0.06	3.61	4.06	4.9	5.56
16	-0.08	3.84	4.38	5.31	6.1
20	-0.1	4.08	4.67	5.76	6.4
24	-0.12	4.42	5.01	6.05	6.74
28	-0.14	4.78	5.37	6.31	7
32	-0.16	5.16	5.63	6.79	7.41
36	-0.18	5.57	6.19	7.14	7.7
40	-0.2	6.01	6.58	7.56	8.08
44	-0.22	5.96	6.94	8.17	8.6
48	-0.24	6.41	7.25	8.36	8.9
52	-0.26	6.65	7.7	8.73	9.11
56	-0.28	7.28	8.15	9.1	9.37
60	-0.3	7.88	8.43	8.83	9.35
64	-0.32	7.75	8.64	8.95	9.49
68	-0.34	8.06	9.06	9.24	9.59

Table A.7 Titration Table for determining the PZC of the peat impregnated with 1.08M Fe

ml of base/ acid added	mequ/g added	pH 1 M NaCl	pH 0.1 M NaCl	pH 0.01 M NaCl	pH 0.001 M NaCl
3	-0.3	1.9	2.1	2	2
2.5	-0.25	2	2.2	2.1	2.1
2	-0.2	2.1	2.3	2.2	2.1
1.5	-0.15	2.3	2.3	2.35	2.3
1	-0.1	2.5	2.6	2.5	2.5
0.5	-0.05	2.7	2.88	2.8	2.8
0	0	3.2	3.2	3.3	3.2
1	0.1	5.3	4.4	4.4	4.7
2	0.2	7	5.8	5.7	6.2
3	0.3	8.2	7.2	7	7.4
4	0.4	9	8.1	7.9	8.4
5	0.5	9.9	8.9	8.7	9.4
6	0.6	10.6	9.7	9.6	10.3
7	0.7	11	10.3	10.2	10.7
8	0.8	11.1	10.9	10.7	11.1

Table A.8 Titration Table for determining the PZC of the peat impregnated with 0.54M Fe

ml of base/ acid added	mequ/g added	pH 1 M NaCl	pH 0.1 M NaCl	pH 0.01 M NaCl	pH 0.001 M NaCl
6	-0.6	1.7	1.8	1.8	1.9
5	-0.5	1.8	1.9	1.9	1.9
4	-0.4	1.9	2	1.9	2
3	-0.3	2	2.1	2.1	2.1
2	-0.2	2.2	2.2	2.2	2.3
1	-0.1	2.5	2.5	2.5	2.5
0	0	3	3.1	3.1	3
1	0.1	3.8	4.1	4	3.9
2	0.2	4.8	5.3	4.9	4.8
3	0.3	5.6	6.2	5.8	5.6
4	0.4	6.5	7.4	6.8	6.6
5	0.5	7.3	8.3	7.6	7.4
6	0.6	8	9	8.3	8.1
7	0.7	8.7	9.7	8.9	8.7
8	0.8	9	10.3	9.5	9.3
9	0.9	9.6	10.8	10	9.9

Table A.9 Titration Table for determining the PZC of the peat impregnated with 0.108M Fe

ml of base/ acid added	mequ/g added	pH 1 M NaCl	pH 0.1 M NaCl	pH 0.01 M NaCl	pH 0.001 M NaCl
6	-0.6	1.9	2	2	2
5	-0.5	2	2.1	2	2.1
4	-0.4	2.1	2.2	2.1	2.2
3	-0.3	2.2	2.3	2.3	2.3
2	-0.2	2.3	2.4	2.4	2.4
1	-0.1	2.4	2.6	2.5	2.5
0	0	2.7	2.8	2.8	2.9
2	0.2	3.6	3.8	3.8	3.9
4	0.4	4.7	4.8	4.9	5
6	0.6	5.7	5.9	6	6.2
8	0.8	6.9	7	7.1	7.4
10	1	8	8.2	8.3	8.7
12	1.2	9	9.3	9.5	10
14	1.4	10	10.4	10.6	11
16	1.6	10.9	11.2	11.3	11.4
18	1.8	11.3	11.5	11.5	11.8

Table A.10 Titration Table for determining the PZC of the peat impregnated with 0.054M Fe

ml of base/ acid added	mequ/g added	pH 1 M NaCl	pH 0.1 M NaCl	pH 0.01 M NaCl	pH 0.001 M NaCl
8	-0.8	1.8	2	1.9	1.9
7	-0.7	1.9	2	2	2
6	-0.6	1.9	2.1	2	2
5	-0.5	2	2.1	2.1	2.2
4	-0.4	2.1	2.2	2.2	2.2
3	-0.3	2.2	2.4	2.3	2.4
2	-0.2	2.3	2.5	2.6	2.6
1	-0.1	2.7	2.8	2.8	2.8
0	0	2.9	3.1	3.1	3.2
2	0.2	3.9	4.2	4.1	4.1
4	0.4	5.1	5.6	5.5	5.4
6	0.6	6.3	7	6.6	6.5
8	0.8	7.5	8	7.7	7.4
10	1	8.4	9.2	8.7	8.3
12	1.2	9.3	10.1	9.8	9.1
14	1.4	10	10.9	10.4	9.8

Table A.11 Detected Metals in peat and their concentrations

Metal	Concentration in ppb (mg/kg)
Fe	1060.0
Mn	28.0
Ni	0.4
Cu	1.4
Zn	63.4
Br	106.7
Pb	3.5

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